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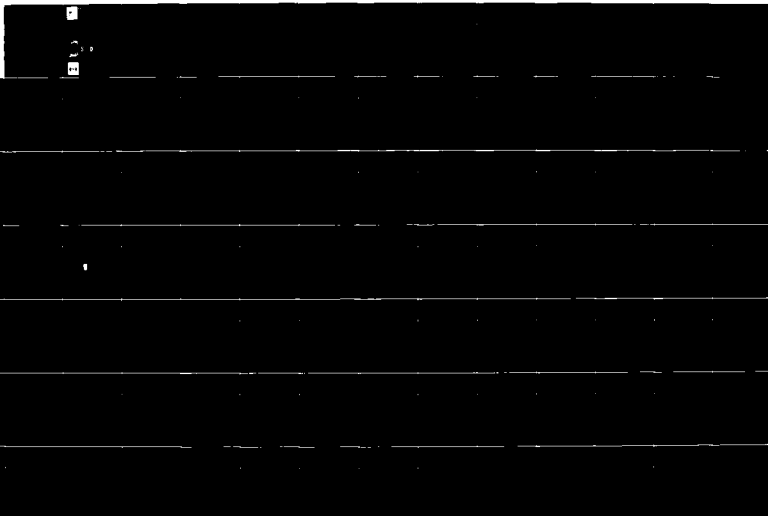
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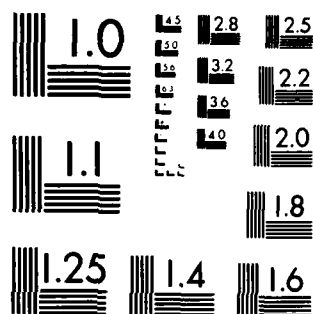
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WATER QUALITY RESEARCH PROGRAM

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RECENT DEVELOPMENTS IN THE ANALYSIS OF METALS IN WATER, WASTEWATER, AND OTHER MATRICES

by

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<p>The analysis of water, wastewater, sediment, and other matrices for the presence of metals has become a large proportion of the work requested from the typical analytical laboratory. Advances in sample preparation, analytical techniques, and equipment capabilities are occurring at a rapid pace. This report is intended to help the working analyst come to grips with the rapidly expanding numbers of methods and techniques for trace metal analysis.</p> <p>The advances in trace metal analysis have been made in two different areas that are the primary focus of this report: better instrumentation (including atomization, nebulization, optics, and data manipulation) and new and novel techniques of sample preparation (preconcentration, matrix removal, and dissolution). These topics are treated in Parts II and III, respectively. As detection limits get lower, contamination and loss of analyte</p> <p style="text-align: right;">(Continued)</p>					
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cont'd during sample preparation and analysis become increasingly significant. This subject is discussed in Part IV. Sources of interference in trace metal analysis, particularly in complex sample matrices that are becoming a larger percentage of the analyst's effort, are discussed in Part V.

To aid the analyst with specific analytical problems, a comprehensive bibliography of pertinent literature from recent journals and periodicals is provided in Appendix A.

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PREFACE

This report was prepared as part of the Water Quality Research and Development Program conducted by the US Army Corps of Engineers. Specifically, preparation of this report was funded by the US Army Corps of Engineers (USACE) under the Analytical Procedures for Water and Wastewater work unit (31766) of the Water Quality Research Program (WQRP).

The work was performed during the period from October 1985 to September 1986 by the Waste Management Research and Education Institute, The University of Tennessee (UT), and the Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES). The work was conducted at WES under the direct supervision of Mr. Norman Francingues, Chief, WSWTG; and the general supervision of Drs. Raymond L. Montgomery, Chief, EED; Jerry Mahloch, WQRP Program Manager; and John Harrison, Chief, EL.

This report was authored by Dr. Larry W. Jones, UT, with contributions from Messrs. M. John Cullinane and Jerry N. Jones, WSWTG, WES. Mr. Jones is presently employed by the R. S. Kerr Laboratory, US Environmental Protection Agency. The USACE Technical Monitor was Ms. Lynn Lamar. Technical reviewers of this report were Dr. James M. Brannon, Aquatic Processes and Effects Group, Ecosystem Research and Simulation Division; Mr. Richard A. Shafer, WSWTG; and Ms. Ann Strong, Chief, Analytical Laboratory Group, EED, WES. The report was edited by Ms. Lee T. Byrne, WES Information Products Division, Information Technology Lab.

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CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENTS

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
atmospheres (standard)	101.325	kilopascals
degrees (angle)	0.01745329	radians
microns	0.001	millimetres
pounds (force) per square inch	6.894757	kilopascals

RECENT DEVELOPMENTS IN THE ANALYSIS OF METALS IN
WATER, WASTEWATER, AND OTHER MATRICES

PART I: INTRODUCTION

Background

1. Metals are naturally occurring elements found in several different forms including dissolved, soluble, complexed, and particulate metals (Plumb 1981). The actual distribution of metals among these forms depends on site-specific environmental chemistry. Important factors in determining the form in which metals will be found include: pH, redox potential, and the presence of complexing molecules. Metals may reach waterways as a result of natural processes such as erosion and/or weathering of geological formations or as a result of man's activities such as mining, milling, and other industrial processes. Once in the waterway, metals are of concern because of their potential for adverse environmental impacts. The nature and severity of these impacts are a function of the metal species, metal concentration, distribution of the metal among the various physical and chemical forms, and sensitivity of the organisms exposed.

2. Analysis of trace metal components in water, wastewater, and other matrices has become a large proportion of the work requested from the typical analytical laboratory and has resulted from recent pressures from public citizens, regulatory agencies, and liability actions. These pressures have increased the numbers of samples that are required for any given site or problem, the parameters for which analyses are required, and the precision and sensitivity to which they must be quantified by several orders of magnitude.

3. The trend to lower and lower detection limits has followed technological advances in two different fields: (a) the highly sophisticated and widely available analytical methods and equipment used for sample manipulation and constituent detection and (b) the new, sensitive methodologies used for mutagenic, carcinogenic, and teratogenic testing of low levels of environmental contaminants. These advances, coupled with the unacceptability of even the smallest environmental health risks by the general public, will

bring about even further emphasis upon precise and accurate measurement of environmental contaminant levels.

4. Although trace metals have always been an integral part of the environment, the rapid industrial development in the last few decades has greatly increased their levels and occurrence. Table 1 illustrates the wide spread presence of relatively high levels of heavy metals in the effluents from several common industries.

Sampling plans and procedures

5. Although not specifically included in the coverage of this manual, sampling plans and procedures are of prime concern to the overall quality of any analytical program. They are a possible source of major errors. The quality and utility of analytical data depend critically on the validity of the sample and the adequacy of the sampling programs. Continuing improvements in analytical methodology allow, and often require, the use of smaller and smaller analytical test portions so that errors in sampling become increasingly significant. As a guideline, Youden (1967) has proposed that when the analytical error is one-third or less of the sampling error, further reduction of the analytical error is of little consequence to overall precision and accuracy. Errors resulting from poor sampling plans and protocols cannot be controlled or corrected by the use of blanks, standards, or reference samples; they reflect only the quality of the sampling operations. Poor sample handling and preservation techniques are common sources of contamination and loss of analyte, as discussed in Part IV.

6. The analyst is often asked to review or interpret proposed sampling plans and procedures and should be knowledgeable of their common problems and pitfalls. An American Chemical Society (ACS) Committee (1983) recommended that an acceptable sampling program should include at least (a) a proper statistical design that takes into account the goals of the studies and its certainties and uncertainties; (b) instructions for sample collection, labeling, preservation, and transport to the analytical facility; and (c) training of personnel in the sampling techniques and procedures specified. These points should be applied to all analyses. These topics have been recently reviewed by Katerman and Pijpers (1981) and Kratochvil, Wallace, and Taylor (1984). An excellent book covering the theory of sampling is that of Cochran (1977). Two excellent US Army Corps of Engineer (CE) publications on the subject were developed during the Environmental Water Quality Operational Studies (EWQOS)

Table 1
Occurrence of Heavy Metals in Selected
Industrial Waste Effluents*

<u>Waste Stream</u>	<u>Ag</u>	<u>As</u>	<u>Cd</u>	<u>Cr</u>	<u>Cu</u>	<u>Fe</u>	<u>Hg</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Se</u>	<u>Ti</u>	<u>Zn</u>
Cooling water				x									
Electronics	x				x						x		
Fertilizers			x	x	x	x	x	x	x	x			
Fibers					x	x							x
General industrial and mining				x	x			x		x			x
Insecticides and pesticides		x			x		x						
Metal plating			x	x	x	x			x	x			x
Municipal solid waste				x	x	x			x			x	x
Paint products				x						x		x	
Paper products				x	x		x		x	x		x	x
Pipe corrosion					x	x				x			
Photographic processing	x			x									
Printing/dyeing				x						x			
Sewage sludge			x		x	x				x			x
Tanning		x		x									

* Adapted from Burrell (1975).

research program: IR E-86-1 "General Guidelines for Monitoring Contaminants in Reservoirs" (Waide 1986) and IR E-87-1 "Sampling Design for Reservoir Water Quality Investigations" (Gaugush 1987).

7. Of particular concern are the sampling of sediments and the determination of the number of samples that should be collected to adequately characterize the area under investigation. Plumb (1981) provides some general concepts on sediment sampling that are also applicable to water sampling. First, in general, the greater the number of samples collected, the better the source will be defined. Second, the mean of a series of replicated measurements is generally less variable than a series of individual measurements. Third, statistics generally require two characteristics, usually the mean and standard deviation. Finally, the number of required samples is proportional to the source heterogeneity.

8. Since these factors do not serve to limit the number of samples required, Plumb (1981) suggests that the number of samples to be collected will depend primarily on the financial resources available for the project. The number of samples that can be collected and analyzed can be determined as follows:

$$NS = \frac{FA - CS - CA}{AC}$$

where

NS = number of samples

FA = funds available

CS = cost of sampling

CA = cost of data interpretation and report preparation

AC = analytical cost per sample

9. Plumb (1981) also suggests a second technique for determining the number of samples based on the level of statistical reliability or confidence.

$$NS = \frac{t^2 s^2}{d^2}$$

where

NS = number of samples

t^2 = Student's t-distribution value

s^2 = population variance

d^2 = statement of margin or error

10. In many cases, funds will not be sufficient to conduct a statistically sound sampling program. In such cases, Plumb (1981) suggests one or more of the following trade-offs:

- a. Reduce the replicate sampling at each station. This will allow the chemical distribution within the project area to be determined, but variability at a single sampling location cannot be calculated.
- b. Maintain replicate sampling but reduce the number of sampling locations. This will result in the project area being less well defined, but sampling variability can be calculated.

- c. Reduce the number of analyses that will be run on each sample. In this way, samples have to be analyzed only for specific parameters of concern in a given project area. Because the analyses to be run are site specific, no mandatory list of analyses can be recommended at this time.
- d. Increase the financial resources available for sample analysis. This will increase the number of samples that can be collected and analyzed.

Definitions

11. The terminology used in the analytical literature has developed different connotations and/or meanings in different segments of the literature. This section clarifies the meanings of several of the terms and abbreviations as used in this report and is, to a large extent, based on the Principles of Environmental Analysis developed by the ACS Committee on Environmental Improvement (1983).

12. Trace and ultratrace analyses. The terms "trace" and "ultratrace analysis" are commonly used but poorly defined in analytical chemistry. There is no hard and fast rule for determining what is trace or ultratrace. Indeed, as analytical techniques become more sophisticated, the definition of each will also change. One possible classification of the ranges of concentration of analyte in a sample is as follows: major constituent if at $>10,000$ ppm (>1 percent); minor, 10 to $10,000$ ppm (0.01 to 1 percent); trace, 0.1 to 10 ppm; and ultratrace, detection limit to 0.1 ppm. Analyses can also be characterized on the basis of the size of the analytical sample. The following classification has been suggested (Zief and Mitchell 1976): macro if the sample is >0.1 g; meso if 0.01 to 0.1 g; micro if 0.001 to 0.01; and submicro if <0.001 g. Analysis of trace elements at the level of ng/g to pg/g has been termed "extreme trace analysis" by Tolg (1987), who reported a critical comparison of new developments in determination methods at these levels.

13. Verification and validation. Verification is the general process used to decide whether a method in question is capable of producing accurate and reliable data. Validation is an experimental process involving external corroboration by other laboratories (internal or external) or methods, or the use of reference materials to evaluate the suitability of a method. Neither addresses the relevance, applicability, usefulness, or legality of an environmental measurement (Taylor 1983). Confirmation, a type of verification, is a process used to assure that the analyte has been detected and measured reliably and acceptably.

14. Sensitivity. Sensitivity reflects the ability to discern the difference between very small amounts of a substance. Given adequate precision, the greater the sensitivity, the better the detectability. A survey of the analytical literature shows clearly that there is a lack of consistency in definition and/or specification of detection limits. It is therefore difficult to make critical sensitivity comparisons between methods for a particular analyte. The US Environmental Protection Agency (USEPA) (1979b) has defined sensitivity for atomic absorption spectrometry (AAS) as: the concentration in milligrams of metal per litre that produces an absorption of 1 percent. Another measure of sensitivity, called Background Equivalent Concentration, is the concentration of an analyte that yields a net intensity signal equal to the intensity of the background.

15. Detection limit. Detection limit indicates the smallest quantity or concentration of a substance that can be detected, often called the "lower limit of detection." The detection limit can be expressed either as an "absolute limit" (the smallest detectable weight of the substance usually expressed in micrograms) or as a "relative limit" (the lowest detectable concentration expressed as a percentage, parts per million on a weight or atomic basis, milligrams per litre, or other concentration units).

16. Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid waste standards would be the signal-to-noise ratio and degree-of-scale expansion used, whereas the latter would be more affected by sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA), as quoted in USEPA (1979a), has approved the following definition for detection limit: "that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to blank absorbance measurement." This definition assumes a relative standard deviation of 50 percent so that results with a precision of 10 percent can be obtained only at values greater than five times the detection limits. Differences in detection limits of up to three times are usually not significant because variations within a given instrument, day-to-day changes, and operator skill can easily alter the values by that amount. The Royal Society of Chemistry, Analytical Methods Committee (1987) has also recommended a standard definition of the detection limit.

17. Accuracy and precision. Accuracy refers to the correctness of the analytical result. Unfortunately, in spite of its importance, there is no general agreement as to how accuracy is evaluated. Inaccuracy results from imprecision (random error) and bias (systematic error) in the measurement process. Unless the true value is known or can be assumed, accuracy cannot be evaluated. Bias can be estimated only from the results of measurements of samples with known composition. Precision reflects only the reproducibility of the analytical result. A method may yield precise but inaccurate results if systematic errors are inherent in the method. Systematic errors may derive from each step in the analytical process, i.e., sampling, pretreatment, and concentration, as well as from the performance of the analysis by different analysts or analytical equipment. High precision does not imply high accuracy and vice versa.

18. Two approaches to reducing systematic errors are empirical calibration methods and statistical methods. Since most analytical methodologies are typically calibrated with synthetic standards of known composition, a reasonably good empirical correction for determinant errors can usually be obtained. If satisfactory standards are not available, then a statistical evaluation of the systematic errors offers the only other objective method of solution. Statistically, this concept is referred to as disposition. The generally accepted statistic for expressing precision or reproducibility is the relative standard deviation, i.e., the percentage ratio of the standard deviation to the mean for a series of measurements. A relative standard deviation of 1 to 3 percent is obtainable under ideal circumstances, but analysis involving extensive pretreatment and complex matrices more typically range from 10 to 25 percent. The attainable precision is affected by the degree of controls over the sample homogeneity, sample delivery, the excitation or absorption process, the dispersing element, and the detector. Maintaining a high degree of control over these analytical procedures is the basis of the rest of the discussion in this manual.

19. Optimum concentration range. A range is defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed (USEPA 1979a).

20. Selectivity. Interferences in trace analysis are a major concern. Quantitative measurement assumes a pure signal derived from the species being measured, so signal sources other than the analyte must be minimized, eliminated, or corrected for. Any signal interference that is not eliminated or detected will have an effect upon the sensitivity and accuracy of the analysis. The sources of interference and the ways to eliminate them are important aspects of trace analysis and are discussed in detail in Part V. The analyst must resort to a variety of methods for achieving adequate selectivity.

21. Dissolved, suspended, and total metals. As defined by USEPA (1979a), dissolved metals are those constituents (metals) that will pass through a 0.45- μ * membrane filter; suspended metals are those constituents (metals) that are retained by a 0.45- μ membrane filter; and total metals are the concentrations of metals determined on an unfiltered sample following vigorous digestion or the sum of the concentrations of metals in both the dissolved and suspended fractions. The term "total recoverable metals" refers to the concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid. For further discussion, see "Speciation of Trace Metals" in Part III.

Quality assurance and quality control

22. Each laboratory should have and use a quality assurance (QA) program. Quality control (QC) is usually defined as those activities performed on a day-to-day basis to ensure that the data being generated are valid. Such activities usually take up a minimum of 10 percent of laboratory efforts and include not only the conducting of spiked and replicate analyses but also the performing of checks and tests on the instrumentation and reagents used in the course of the analytical process. See Provost and Elder (1985) for a discussion of how to choose cost-effective QA/QC programs for the analytical laboratory.

23. Control plots. The attainment of statistical control is the first requirement that must be met before an assessment of accuracy can be made. For this purpose, the establishment of a system of control charts is a basic principle (ACS 1983). Control charts are plots of multiple data points from the same or similar samples or processes versus time (American Society for

* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 4.

Testing and Materials (ASTM) 1976). They are used to determine if a system is in a state of statistical control. Control charts should be used to monitor or visualize the relative variability of repetitive data and as a means of assessing the accuracy of measurements when used with reference materials, spiked samples, and/or analysis of surrogates. The attainment of statistical control is the first requirement that must be met before assessment of accuracy can be made.

24. Audits. Audits should be a feature of all QA programs. A system audit should be made at appropriate intervals to assure that all aspects of the QA program are operative. Performance audits, evaluation based on the results of blind, standard samples, also provide valuable quality assessment information. Participation in interlaboratory and collaborative test programs should also be used to assess the quality of analytical data.

25. Repeatability. Repeatability generally describes the variation in data generated from a single sample over a short period of time. Reproducibility refers to variability over an extended period of time and/or by various analysts or laboratories. Intralaboratory variability refers to the difference in results when a single laboratory measures portions of the same sample repeatedly; interlaboratory variability refers to the difference of results obtained by different laboratories when measuring portions of a common sample.

26. Reagent blanks. Each individual reagent used in the analytical procedure should be tested to determine whether it causes any interference with the analysis. The conditions for handling and analyzing the blank should be identical to that used in the analysis. The reagent blank should be analyzed with each new reagent, and the data generated from the reagent blank should be documented.

27. Method blank. The method blank is analyzed to determine whether the cumulative effect of the reagents causes interference with the analysis. The method blank consists of only laboratory pure water and the reagents used in the analysis. A method blank should be analyzed in the same manner as standards and samples each time an analysis is conducted.

28. Field blanks and control sites. Analysis of a sample from a similar source that is not contaminated with or does not contain the analyte(s) in question are usually called field blanks. When environmental measurements are made to investigate localized contamination (e.g., at a hazardous waste site

or point source discharge), measurements of concentrations at sites recognized as uncontaminated (control sites) are usually required to determine the extent and seriousness of the suspected contamination. Such sites must be chosen carefully, and the number of samples must be optimized to establish the significance of any differences found.

29. Replicate analyses. A minimum of 5 percent of all samples being analyzed should be tested in replicate. Replicate samples are prepared by dividing a homogeneous sample into separate parts so that each part is also homogeneous and representative of the original sample. The data obtained from the replicate analyses should be used to document the precision of that particular method.

30. Spiked analyses. A minimum of 5 percent of all samples being analyzed should be analyzed as spiked samples. Spiked analyses are performed by splitting a sample into replicates; then, to one of the replicates, a known amount of the contaminate being tested for is added. The amount of the contaminate being added should be approximately the same amount present in the unspiked sample. Both samples should then be analyzed, and the percentage recovery (R) of the spike should be expressed as: $R = 100(F - I)/A$, where F is the analytical result of the spiked sample, I is the result before spiking of the sample, and A is the amount of the contaminant added to the sample. This information should be documented.

31. Chain of custody. In instances where the data generated may be used in a court of law, the laboratory should establish a set of protocols designed to ensure and document the integrity and custody of the samples. The chain of custody should begin with the receipt of the sample and continue through the analytical process and consist of the following:

- a. Date and time the laboratory received custody of the sample.
- b. Person accepting custody of the sample.
- c. Preservation used on the sample.
- d. Date and time of the analysis of the sample.
- e. Person(s) performing the analysis.
- f. The type of analysis and analytical technique performed.

Once completed, the chain-of-custody form should be attached to the analytical report and forwarded to the sampling agency.

Documentation and reporting

32. Documentation of analytical measurements should provide information sufficient to support all claims made for all the results. It requires all information necessary to:

- a. Trace the sample from the field to the final result.
- b. Describe the methodology used.
- c. Describe the confirmatory evidence.
- d. Support statements about detectability.
- e. Describe the QA/QC program and demonstrate adherence to it.
- f. Support confidence statements for the data.

Laboratory records should be retained in a permanent file for a length of time set by government, or other legal requirements, or by the employing institution, whichever is longest.

33. Electronic data processing must be tested periodically with known data to show that it is carrying out procedures as required. Results of such testing should be included in the documentation.

34. The analyst is responsible for fully describing and interpreting the data and reporting it in an appropriate manner. Results should be stated in such a way that their significance is understood by the client, the public, and any legal authorities. It is important to emphasize that the most important characteristic of any analytical result is an adequate statement of its uncertainty interval. If average values are reported, an expression of the precision and number of measurements must be included. Sufficient information should be included so that the ultimate users of the data can understand the interpretations and conclusions without having to make their own interpretations from raw data.

Costs

35. The price or cost of analyzing samples is an important factor in the development of a comprehensive environmental evaluation process. Unit costs for the determination of metals will vary geographically and are normally a function of the number of analyses requested at any one time. Special discounts are often offered where a large number of samples are submitted at one time and/or for prompt payment. Typical analytical costs for metals analysis are presented in Table 2. These costs are for analysis only and do not include sample digestion if required. The extreme range of unit costs is attributed to the large price breaks that analytical laboratories give for

Table 2
Analytical Costs by Parameter

<u>Parameter</u>	<u>Range of Cost</u>
Aluminum	\$ 4.00 - 20.00
Antimony	5.00 - 35.00
Arsenic	6.00 - 35.00
Barium	4.00 - 20.00
Beryllium	4.00 - 20.00
Boron	7.00 - 35.00
Cadmium	2.50 - 16.50
Calcium	2.00 - 20.00
Carbon	5.00 - 35.00
Carbonates	3.00 - 15.00
Chromate	3.00 - 16.50
Chromium	4.00 - 20.00
Cobalt	4.00 - 9.30
Copper	2.50 - 20.00
Cyanide	5.00 - 40.00
Fluorides	3.50 - 25.00
Iron	2.50 - 20.00
Lead	2.50 - 20.00
Magnesium	4.00 - 20.00
Manganese	2.50 - 20.00
Mercury	11.00 - 35.00
Molybdenum	4.00 - 20.00
Nickel	2.50 - 20.00
Selenium	5.00 - 55.00
Silica	4.00 - 20.00
Silver	4.00 - 20.00
Sodium	2.00 - 20.00
Strontium	4.00 - 75.00
Thallium	4.00 - 20.00
Tin	2.50 - 20.00
Vanadium	4.00 - 30.00
Zirconium	10.00 - 35.00
Zinc	2.50 - 20.00

quantity discounts, i.e., the more samples submitted at any one time, the lower the unit cost.

Purpose and Organization

36. This manual is intended to help the working analyst come to grips with the rapidly expanding numbers of methods and techniques for trace metal

analysis. Advances in sample preparation, analytical techniques, and equipment capabilities are occurring at a rapid rate. The majority of the new techniques included in this report have been developed since 1981.

37. The advances in trace analysis have been made in two different areas that are the primary focus of this report: better instrumentation (including atomization, nebulization, optics, and data manipulation) and new and novel techniques of sample preparation (preconcentration, matrix removal, and dissolution). These topics are treated in Parts II and III, respectively. As detection limits get lower and lower, contamination and loss of analyte during sample preparation and analysis become increasingly significant (see Part IV). Sources of interference involved with metal analysis in the difficult and complex sample matrices that are becoming an increasing proportion of the analyst's effort are the topic of Part V.

38. The rapid advances and the number of reports that deal with specific trace metals or analytical techniques make generalizations about specific methodologies or techniques difficult or impossible. The literature is full of procedures and techniques directed toward problems with low levels of specific metals and/or particular equipment modifications. To aid the working analyst with specific analytical problems, a bibliography of pertinent literature found in commonly available, recent journals and periodicals is provided in Appendix A. The listing is cataloged by the specific metal(s) and analytical techniques discussed in the paper or report.

PART II: CURRENT OPTIONS FOR TRACE METAL ANALYSIS

39. The increasing awareness of the importance of trace amounts of metals in biological systems and recent regulatory pressures have greatly stimulated the refinement and sensitivity of analytical equipment. Indeed, as detection limits have gotten lower, regulatory requirements have followed and now call for metal concentrations at levels that could not be analyzed only a few years ago.

40. Part II summarizes some of the innovations in analytical equipment and hardware that have become the standards in the analytical community during the last few years. Some of the areas where innovations are likely to have profound influence upon the analysis of trace metals are automatic sample injection (ASI) and multiple metal analysis in AAS and atomic emission spectrometry (AES) systems, ion chromatographic techniques, and rapid, field-type colorimetric methods. A certain amount of material covered in this part is necessarily rudimentary to many readers. It should be pointed out that no single technique will provide all of the analytical capability required to provide comprehensive analytical data for trace metal measurements. The analyst must carefully assess the analytical requirements and then choose methodology and instrumentation that will provide data of sufficient accuracy, precision, and sensitivity to solve analytical problems.

41. The USEPA (1986) has developed a list of approved test procedures for 75 parameters commonly measured in environmental samples. The approved test procedures for trace metals are listed in Table 3. A variety of methods have been approved for all of the metals included in this manual. Most of these methods are summarized in this chapter.

Spectroscopic Instrumental Methods

42. Spectroscopic methods can be broken into two major categories: those depending upon analyte light absorption and those depending upon its emission or fluorescence. The general method covers the entire electromagnetic spectrum ranging from very energetic, short-wavelength gamma rays to the far infrared region. All methods require a spectrometer that allows a discrete band or wavelength region to be separated from the general spectrum. The specificity and sensitivity of the determination are usually established

Table 3

List of Inorganic Test Procedures Approved by USEPA (1986)

Parameter units, mg/l ²	Method	Reference (Method No. or Page)			
		USEPA 1979a	APHA (1985)*	ASTM (1985)*	USGS**
Arsenic + Total ²	Digestion ² followed by atomic absorption (AA)	206.5	----	-----	-----
	gaseous hydride, AA	206.3	303E	D2972-84 (B)	I-3062-84
	furnace, inductively coupled plasma, or	206.2	304	-----	-----
	colorimetric (SDDC)	-----	-----	-----	200.7 ²
Barium - Total ²	Digestion ² followed by AA direct aspiration	206.4	307B	D2972-84 (A)	I-3060-84
	AA furnace or	208.1	303C	-----	I-3084-84
	inductively coupled plasma	208.2	304	-----	-----
		-----	-----	-----	200.7 ²
Beryllium - Total ²	Digestion ² followed by AA direct aspiration,	210.1	303C	D3654-84 (A)	I-3095-84
	AA furnace,	210.2	304	-----	-----
	inductively coupled plasma, or	-----	-----	-----	200.7 ²
	colorimetric (aluminon)	-----	309B	-----	-----

(Continued)

* APHA = American Public Health Association; ASTM = American Society for Testing and Materials.

** "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," US Department of the Interior, US Geological Survey, Open File Report 85-495, 1986, unless otherwise stated.

† See notes at end of table.

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Table 3 (Continued)

Parameter units, mg/l	Method	Reference (Method No. or Page)				
		USEPA 1979a	APHA (1985)*	ASTM (1985)*	USGS**	Other†
Cadmium - Total ²	Digestion ² followed by AA direct aspiration	213.1	303A or B	D3557-84(A or B)	I-3135-84 or I-3136-84	33.089 ⁶ p.37 ³
	AA furnace, inductively coupled plasma, ⁵ voltametry, or colorimetric (dithizone)	213.2	304	-----	-----	-----
		-----	-----	-----	-----	200.7 ²
Chromium VI - dissolved,	0.45-µm filtration followed by AA chelation-extraction, or colorimetric (diphenylcarbazide)	218.4	303B	-----	I-1232-84	-----
		-----	-----	-----	I-1230-84	307B ⁵
	Digestion ² followed by AA direct aspiration, AA chelation- extraction	218.1	303A	D1687-84(D)	I-3236-84	33.089 ⁶
Chromium - Total ²	AA furnace, inductively coupled plasma, or colorimetric (diphenylcarbazide)	218.3 218.2	303B 304	----- -----	----- -----	-----
		-----	-----	-----	-----	200.7 ²
		-----	312B	D1687-84(A)	-----	-----
Copper - Total ²	Digestion ² followed by AA direct aspiration	220.1	303A or B	D1688-84(D or E)	I-3270-84 or I-3271-84	33.089 ⁶ p.37 ³

(Continued)

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Table 3 (Continued)

Parameter units, mg/l	Method	Reference (Method No. or Page)			
		USEPA 1979a	APHA (1985)*	ASTM (1985)*	USGS**
Iron - Total ²	AA furnace, inductively coupled plasma, colorimetric (neocuproine), or (bichinchoninate)	220.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	313B	D1688-84(A)	-----
		-----	-----	-----	Note 7
	Digestion ² followed by AA direct aspiration,	236.1	303A or B	D1068-84(C or D)	I-3381-84
	AA furnace, inductively coupled plasma, or colorimetric (phenanthroline)	236.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	315B	D1068-84(A)	-----
Lead - Total ²	Digestion ² followed by AA direct aspiration	239.1	303A or B	D3559-85(A or B)	I-3399-84
	AA furnace, inductively coupled plasma, voltage ⁵ , or colorimetric (dithizone)	239.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	316B	D3559-85(C)	-----
Manganese - Total ²	Digestion ² followed by AA direct aspiration,	243.1	303A or B	D858-84(B or C)	I-3454-84
	AA furnace, inductively coupled plasma, or colorimetric (persulfate), or (periodate)	243.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	319B	D858-84(A)	-----
		-----	-----	-----	33.126 ⁶ Note 9

(Continued)

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Table 3 (Continued)

Parameter units, mg/l	Method	Reference (Method No. or Page)			
		USEPA 1979a	APHA (1985)*	ASTM (1985)*	USGS**
Mercury - Total ²	Cold vapor, manual or automated ²	245.1	303F	D3223-80	I-3462-84
Nickel - Total ²	Digestion ² followed by AA direct aspiration	245.2	----	-----	-----
	AA furnace, inductively coupled plasma, or colorimetric (hiptoxime)	249.1	303A or B	D1886-84(C or D)	I-3499-84
		249.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	321B	-----	-----
Selenium - Total ²	Digestion ² followed by AA furnace, inductively coupled plasma, or AA gaseous hydride	270.2	304	-----	-----
		-----	-----	-----	200.7 ²
		270.3	303E	D3859-84(A)	I-3667-84
Silver - Total ¹¹	Digestion ² followed by AA direct aspiration, AA furnace, colorimetric (dithizone), or inductively coupled plasma	272.1	303A or B	-----	I-3720-84
		272.2	304	-----	-----
		-----	-----	-----	319B ⁵
		-----	-----	-----	200.7 ²
Zinc - Total ²	Digestion ² followed by AA direct aspiration, AA furnace, inductively coupled plasma, or colorimetric (dithizone) or (zincon)	289.1	303A or B	D1691-84(C or D)	I-3900-84
		289.2	304	-----	-----
		-----	-----	-----	200.7 ²
		-----	328C	-----	-----
		-----	-----	-----	Note 11

(Continued)

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Table 3 (Continued)

Notes:

1. For the determination of total metals, the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes" (USEPA 1979a). One (Section 4.1.3) is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (Section 4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all sample types. Particularly if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred, making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion. In all cases, the method write-up should be consulted for specific instruction and/or cautions.

NOTE: If the digestion included in one of the other approved references is different from the above, the USEPA procedure must be used.

Dissolved metals are defined as those constituents that will pass through a 0.45- μ m membrane filter. Following filtration of the sample, the reference procedure for total metals must be followed. Sample digestion for dissolved metals may be omitted for AA (direct aspiration or graphite furnace) and inductively coupled argon plasma (ICP) analyses, provided the sample solution to be analyzed meets the following criteria:

- a. Has a low chemical oxygen demand (COD) (<20).
- b. Is visibly transparent with a turbidity measurement of 1 Nephelometric Turbidity Unit (NTU) or less.
- c. Is colorless with no perceptible odor.
- d. Is of one liquid phase and free of particulate or suspended matter following acidification.

2. The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," is given in Appendix C of 40CFR Part 136.

3. American National Standard on Photographic Processing Effluents, 2 April 1975. Available from ANSI, 1430 Broadway, New York, NY 10018.

(Continued)

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Table 3 (Concluded)

4. The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.
5. The approved method is that cited in "Standard Methods for the Examination of Water and Wastewater," 14th Edition, (APHA 1976).
6. "Official Methods of Analysis of the Association of Official Analytical Chemists," 1985, methods manual, 14th Edition.
7. "Copper, Biocinchonate Method, Method 8506," Hach Handbook of Water Analysis, 1979, Hach Chemical Company, PO Box 389, Loveland, CO 80537.
8. "Iron, 1,10-Phenanthroline Method, Method 8008," 1980, Hach Chemical Company, PO Box 389, Loveland, CO 80537.
9. "Manganese, Periodate Oxidation Method, Method 8034," Hach Handbook of Water Analysis, 1979, Hach Chemical Company, Loveland, CO 80537, pp 2-113 and 2-117.
10. Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/l and above are inadequate where silver exists as an inorganic halide. Silver halides such as bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/l, 20 ml of sample should be diluted to 100 ml by adding 40 ml each of 2 M $\text{Na}_2\text{S}_2\text{O}_3$ and 2 M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/l the approved method is satisfactory.
11. "Zinc, Zincon Method, Method 8009," Hach Handbook of Water Analysis, 1979, Hach Chemical Company, Loveland, CO 80537, pp 2-231 and 2-333.

by the instrument's ability to differentiate between these separated wavelength regions. By isolating multiple discrete bands, simultaneous analysis of several analyses can be performed.

Molecular absorption spectrometry (MAS)

43. The oldest and most common spectroscopic method, termed "colorimetric" in Table 3, relies upon the absorption of a molecular species in the ultraviolet, visible, or infrared spectral regions. This technique has been the mainstay of metal analysis. Early measurements were made with crude filters in a colorimeter. Increasing sophistication of the spectral control, measurement sensitivity, and complexing chemicals has kept these methods in the picture, especially for rapid, field testing procedures. Standard Methods (APHA 1985) colorimetric tests have been approved by the USEPA (1986) for determination of As, Be, Cd, Cr(VI), Cr, Cu, Pb, Mn, Ni, Ag, and Zn.

44. The broad absorption bands found for most metal complexes present a major problem that makes their separation difficult, limits sensitivity, and makes interferences a major problem. To provide accurate, quantitative analyses, preliminary chemical separations, masking reactions, or careful control over analysis conditions is required. For example, the common complexing agent dithiozone will complex with as many as 17 other trace metals, making solvent extraction, selective precipitation, or other separation techniques necessary for accurate measurements (Minear et al. 1975).

45. Quantification is based on adherence to Beer's Law, which relates concentration linearly to absorbance by the analyte. This assumes that the analyte is in true solution without other interfering species or particulates. Usually Beer's Law is obeyed when analyte concentrations remain below 1 mmol. The sensitivity of the determination of trace elements varies between metals, but most can be determined directly in the intermediate microgram-per-litre range. Several automated instruments using this technique, which can analyze up to 60 samples/hr, are commercially available. A complete review of colorimetric methods for trace metal analysis is given by Sandell and Onishi (1978) and Hach Company (1987).

Atomic absorption spectrometry (AAS)

46. The most universally available instrument for the analysis of metals is an atomic absorption spectrophotometer. This instrument provides a method that is relatively free from spectral or radiation interferences because each metal has its own characteristic absorption wavelength. The

method is more sensitive than most colorimetric analysis techniques and can also be extended by graphite furnace atomization or sample concentration techniques. An excellent recent review of AAS is given by Magyar (1987).

47. AAS differs from MAS by the fact that the absorbing species is dissociated into the atomic state. Specificity is based upon the fact that the source of radiation absorbed is usually a low-pressure arc lamp containing the element to be analyzed, a hollow cathode, or discharge lamp. The ground state atoms of the analyte selectively absorb the line radiation from the lamp, which gives the method its selectivity and sensitivity. To differentiate emission from absorption processes, the measuring beam is usually pulsed or chopped at a frequency to which the sensing electronics are precisely tuned, thus eliminating most of the background radiation. A complete literature review on Atomic Absorption (AA) Analysis is contained in the two volume set by Varma (1984).

48. Major variations in the AAS methodology revolve around the method by which the analyte is atomized. The most common is the long path-length flame (typically 10 cm) using either an air-acetylene flame that reaches about 2,300° C or the nitrous oxide-acetylene flame at a higher 2,900° C. The former is used primarily for metals that form molecular species of intermediate stability which almost totally dissociate at the lower flame temperature. The hotter flame is used to atomize the metals that characteristically form the harder to dissociate refractory species such as V or Mo. A low-temperature flame (1,850° C) -- the argon-hydrogen-entrained-air flame -- is used for atomizing easily dissociated compounds such as As, Se, and Zn by hydride generation (Burrell 1975).

49. Before atomization in either flame, liquid samples are transformed into an aerosol by one of several types of nebulizers. The aerosol, or a portion of it, is injected into the gas stream, where it is combusted and atomized. A steady-state signal is generated for as long as the sample is being nebulized. The signal is read on a meter or a strip chart or is directly input into a computer interface. The amplitude of this signal, which is directly proportional to the level of analyte in the sample stream, is compared with a known sample signal to determine the level of analyte in the sample.

50. Other types of sample introduction techniques include the Delves cup or tantalum boat method (Minear et al. 1975); in this method, the sample is

placed in the cup, which is then atomized directly in the flame. The electrothermal approach, sometimes referred to as the Massman or L'vov graphite furnace, the Woodruff isothermal furnace, or the carbon rod (Burrell 1975), atomizes the sample by passing an electric current through the graphite sample holder (the furnace). Careful control of the atomizer current gives precise control of the furnace temperature and heating rate, which can be increased in a stepwise fashion to evaporate the solvent, char or ash the sample (which reduces potential interfering materials), and then atomize the analyte. In the Woodruff furnace, the rod is continuously heated at a constant temperature, and the sample is introduced by a quick insertion technique. In either case, the electrothermal cell is placed in the light path so that a transient signal is produced when the sample is atomized.

51. The L'vov platform is a small boat of solid pyrolytic graphite positioned inside the graphite furnace. A slight depression in the center holds about 50 μ l of sample. The furnace is operated at a constant temperature so that when the platform is introduced, it is heated by radiant energy from the furnace walls. A time lag between heating the tube and the platforms permits sample vaporization into a gas atmosphere that is at a higher temperature, which produces a more complete formation of free atoms and reduces interferences. It is especially useful for the determination of highly volatile elements such as Pb, Ca, and As, but is applicable to most elements (Perkin-Elmer 1981).

52. Allied Analytical Systems (1985) has also developed a delayed-action cuvette (DAC), which has a thicker, cooler center region to delay atomization so that it occurs in a higher temperature environment. The DAC is said to incorporate the benefits of the L'vov platform into a single cuvette. The design is claimed to reduce what are regarded as vapor-phase interferences (see Part V) and to have detection limits as much as two orders of magnitude better than flame AA.

53. In the cold vapor technique for mercury, mercuric ion is reduced to metallic mercury with a strong reducing agent such as stannous chloride. The elemental mercury vapor is sparged from the solution with nitrogen gas and passed through a long path-length quartz cell positioned in the light path. Again, a transient signal that is proportional to the amount of mercury in the sample is produced.

54. Table 4 lists the relative detection capabilities for both flame and nonflame techniques. Electrothermal (nonflame) techniques generally have lower detection limits and can use smaller volume samples than those using the flame because a greater percentage of available analyte atoms are vaporized and dissociated in the furnace than in the flame. However, the flame methods are usually much simpler and, because of the higher concentration levels, do not require the standard addition approach to ensure usable accuracy. Table 5 compares the USEPA (1979a) published concentration ranges for AAS by direct sample aspiration and by furnace procedures. USEPA states that these numbers are not contrived and should be obtainable with any satisfactory atomic absorption spectrophotometer.

55. AAS was originally touted by instrument manufacturers as being interference free. However, complex samples such as sludges and sediments often show numerous interferences that can distort the accuracy of the method. Examples of AAS interference and methods to overcome them are given in Part V. Atomic emission spectrometry (AES)

56. AES involves the measurement of the emission of the analyte in the ultraviolet, visible, and near infrared regions. This emission is induced by the use of flame, arc, spark, or plasma. The principle of atomic emission can be thought of as the reverse of atomic absorption in that the excited atom

Table 4
Comparison of Typical Detection Limits for Selected
Atomic Absorption Spectrographic Techniques*

Element	Wavelength nm	Detection Limits (ng/ml)			
		Flame	Furnace	Carbon Rod	Filament
Ag	328.1	0.5	0.003	0.04	0.2
Cd	228.8	0.6	0.001	0.02	0.1
Co	240.7	5	0.04	1	6
Cr	357.9	3	0.05	1	5
Cu	324.7	2	0.01	1	7
Fe	248.3	5	0.03	0.6	3
Mn	279.5	2	0.01	0.1	0.5
Ni	232.0	5	0.1	2	10
Pb	283.3	10	0.06	1	5
Zn	213.9	2	0.0006	0.02	0.08

* Taken from Taylor (1982).

Table 5
Atomic Absorption Concentration Ranges* **

Metal	Direct Aspiration			Furnace Procedure † ††	
	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l	Detection Limit µg/l	Optimum Concentration Range µg/l
Arsenic ‡	0.0002	--	0.0002- 0.02	1	5 - 100
Barium(p)	0.1	0.4	1 - 20	2	10 - 200
Beryllium	0.005	0.025	0.05 - 2	0.2	1 - 30
Cadmium	0.005	0.025	0.05 - 2	0.1	0.5- 10
Chromium	0.05	0.25	0.5 - 10	1	5 - 100
Copper	0.02	0.1	0.2 - 5	1	5 - 100
Iron	0.03	0.12	0.3 - 5	1	5 - 100
Lead	0.1	0.5	1 - 20	1	5 - 100
Manganese	0.01	0.05	0.1 - 3	0.2	1 - 30
Mercury ‡ ‡	0.0002	--	0.0002- 0.01	--	-- --
Nickel(p)	0.04	0.15	0.3 - 5	1	5 - 100
Selenium	0.002	--	0.002 - 0.02	2	5 - 100
Silver	0.01	0.06	0.1 - 4	0.2	1 - 25
Zinc	0.005	0.02	0.05 - 1	0.05	0.2- 4

* Taken from USEPA (1979a).

** The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

† For furnace sensitivity values, consult instrument operating manual.

†† The listed furnace values are those expected when using a 20 µl injection and normal gas flow except in the case of arsenic and selenium, where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

‡ Gaseous hydride method.

‡‡ Cold vapor technique.

produces radiation at several resonant frequencies. Simultaneous multielement determination with detection limits in the low µg/l range is easily achieved with AES.

57. Samples are vaporized, atomized, and excited by the source of the spectrometer. The resulting atomic, ionic, and molecular radiation is focused on the entrance slit of the spectrometer, which is set to the correct wavelength for the atoms being measured. Determination of all of the lines present in the source gives a qualitative measure of all of the elements present.

The intensity of each emission line is directly proportional to the amount of the element present in the source.

58. For a flame source, a very hot, point source flame is usually used to prevent self-absorption from the atoms in the cooler portions of the flame. Oxyhydrogen or oxyacetylene is usually chosen for the flame. Solution samples are directly nebulized into the flame, where desolvation, atomization, and excitation occurs. Multielement analysis has not been commonly employed with flame instruments, which are usually used as single element machines with a monochromator and a single electronic readout. Table 6 lists some of the detection limits typical for flame instruments. For many elements, detection limits are competitive with those obtained for atomic absorption determinations. Flame emission does not require the use of expensive hollow cathode lamps, but total consumption burners are often very noisy and unpleasant to operate.

59. Direct-current (DC) arc optical emission spectrometry has been a classical technique for multielement trace analysis when used with photographic film or plate detection. Most DC arc machines use direct-reading multielement spectrometers. DC excitation requires that a solid sample be placed in a graphite cup, where it is volatilized, atomized, and excited by an arc discharge struck to a graphite counter electrode. DC's as high as 30 amp

Table 6
Typical Detection Limits of Flame Atomic Spectrometric Techniques*

<u>Element</u>	<u>Detection Limits (ng/ml)</u>		
	<u>Absorption</u>	<u>Emission</u>	<u>Fluorescence</u>
Ag	0.5	20	0.1
Cd	0.6	200	0.003
Co	5	50	5
Cr	3	5	50
Cu	2	10	1
Fe	5	50	8
Mn	2	5	1
Mo	100	160	460
Ni	5	30	3
Pb	10	200	10
Zn	2	500	0.02

* Taken from Taylor (1982).

can be used to maintain the discharge. Controlled atmospheres can be used to improve the sensitivity and reduce interferences from entrained air in the discharge. Often the sample is mixed with salts such as lithium fluoride or gallium oxide to improve the stability of the arc and to act as a carrier to sweep the analyte elements into the discharge at a controlled rate.

60. Water samples are prepared for DC arc analysis by evaporating a large sample to dryness and thoroughly mixing with an electrically conducting substrate such as graphite. The evaporation step offers a very large preconcentration step and hence high sensitivity for a wide variety of elements. Major disadvantages of the DC arc are that sample preparation is lengthy and a major source of contamination, the precision of determinations are usually no better than about 20 percent, and the photographic process used to achieve an analysis of up to 40 elements requires a high degree of operator skill and extended time. However, the technique can be rapidly employed for semiquantitative analyses.

61. A high-voltage, alternating current (AC) spark can be used in place of the DC arc to volatilize and excite the analyte elements. Much higher precision is obtained with the AC spark than with the DC arc but with some corresponding loss in sensitivity. For water analysis, either a porous cup electrode or a rotating disk electrode is used. A porous graphite cup absorbs the sample and forms a homogeneous electrode that is atomized and excited by the spark to the counter electrode. In the other technique, a small graphite disk is rotated at a constant speed so that the bottom of the disk is in contact with a small reservoir of the sample. Thus, when the disk rotates, it is continually refreshing the sample on the surface of the disk. The electrical spark to the counter electrode at the top of the disk again atomizes and excites the analyte atoms in front of the spectrometer. Long exposure times can be used with the rotating disk so that very high precision can be realized; however, analysis of multiple samples is very time consuming.

62. Plasma sources come in three types: ICP, the DC argon plasma (DCP), and microwave-induced plasma using both helium and argon. In all cases, solution samples are injected directly as an aerosol similar to flame analysis. Within the plasma, elements exist in a dynamic state between the atom and ion state. Electrons generated in the presence of an easily ionizable element such as Na can shift this equilibrium and cause offsetting changes in atom and ion emission leading to ionization interference (Arellano,

Routh, and Dalager 1985). Several comparisons have been made between the different plasma sources (Broekaert, Leis, and Lagua 1981; Taylor 1981; Worthington 1985). All three sources have benefits over other AES sources, but of the three, ICP appears to have the greatest accuracy and ease of handling. ICP has been increasing in popularity in the past few years. In it, the excitation of the analyte elements is by collision with highly energetic electrons and argon ions in the plasma, which is sustained by a radio-frequency electromagnetic field typically operating at about 27 MHz. The field is coupled to the plasma by a two- or three-turn coil producing a fireball in the argon and sample aerosol having a thermal temperature of about 10,000° K just above the coil. The effective temperature is even higher.

63. Advantages of the ICP include the essentially complete excitation of all atoms in the sample, which gives the capability for high sensitivity and simultaneous measurement of a variety of metals and nonmetals. The linear dynamic range is often 10^4 to 10^6 orders of magnitude, and the detection limits for most elements are better than those of traditional AAS but less than those of graphite furnace AA (Worthington 1985, Routh et al. 1987). The use of a direct-reading computer-controlled spectrophotometer allows the computer to carry out interelement interference corrections prior to printing out the concentrations (Berman, McLaren, and Russel 1981). The higher temperature of the source also greatly contributes to the reduction of interference effects such as molecular compound formation and precludes any need to buffer the sample. Dahlquist and Knoll (1978) give complete analytical methods for simultaneously measuring 5 major elements (Na, K, P, Ca, and Mg) and 14 trace elements (Fe, Cu, Zn, Mn, Pb, Cd, Co, Cr, Ni, V, Ti, Al, Sr, and Ba) in biological tissues and soil with ICP-AES using one set of conditions and a single, mixed standard. The lack of internal electrodes removes any chances of contamination from this source. Ion lines are more prevalent in the spectrum, which is usually less complex than in arc or spark emission spectra. For this reason, different wavelengths are usually used for ICP analysis. Automation of the technique is very straightforward, and analyses can be carried out at a very high rate. Table 7 gives the wavelengths and detection limits suggested by the USEPA (1979b).

64. Although the ICP has several advantages over the DCP, the technique also has several disadvantages. The ICP jet is prone to clogging. Samples must be filtered, and when contaminants are analyzed in saltwater matrices,

Table 7
Recommended Wavelengths and Estimated Instrumental
Detection Limits*

<u>Element</u>	<u>Wavelength</u> <u>nm</u>	<u>Detection Limit</u> <u>ng/ml</u>
As	193.7	53
Ba	455.5	2
Be	313.0	0.3
Cd	226.5	4
Cr	267.7	7
Cu	324.7	6
Fe	259.9	7
Pb	220.3	42
Mn	257.6	2
Ni	231.6	15
Se	196.0	75
Ag	328.0	7
Zn	213.8	2

* The estimated instrumental detection limits are taken from "Inductively Coupled Plasma--Optical Emission Spectroscopy Prominent Lines," (USEPA 1979b).

the instrument must be rinsed between samples to prevent clogging. Although the ICP is generally more expensive than the DCP, it is more popular because it is available from a variety of manufacturers, whereas to date the DCP is available from only one manufacturer.

65. The DCP, or "plasma jet," has more recently been developed commercially for multielement analysis. The DC argon plasma is produced by passing purified argon gas over a cathode and anode between which a DC current is passed, giving a V-shaped discharge. The excitation process is thought to be quite different from that of the ICP. The advent of graphite electrodes that erode very slowly and add very little contamination and of the three-electrode torch (two cathodes and one anode) has increased the facility and usability of the method. For some metals, the DCP technique does not have quite as low a detection capability as ICP, but the detection limits are satisfactory for most trace metal analyses (ASTM 1985). The DCP is believed to accept higher solids concentrations than the ICP and is less sensitive to differences in acid concentration (Worthington 1985). DCP was used to analyze drilling muds in seawater (Gilbert, Liss, and Stacey 1981); salt buffering was used to mask

enhancement effects, and spectral interferences were evaluated using wavelength scanning techniques.

66. All commercial DCP's (and some ICP's) have Echelle gratings. The emitted light is passed through a prism before striking the diffraction grating resulting in a bidimensional or raster spectrum. The Echelle has better resolution than other spectrophotometers and can be used in the manual sequential, rapid sequential, or simultaneous mode.

Atomic fluorescence spectrophotometry (AFS)

67. AFS uses essentially the same instrumentation as AAS. The hollow cathode or discharge lamp is focused at the flame at 90 deg to the spectrometer optical path so that only the light emitted by the nebulized atoms in the flame that are excited and reemit fluorescence will be detected (other than the steady-flame background). Burrell (1975) has reported that detection limits are superior for many elements to those for comparable AAS. This technique is not widely used, and at present, only one commercial machine is available. However, the simplicity of the instrumentation might recommend it for selected applications.

X-ray fluorescence (XRF)

68. XRF is based upon the measurement of stimulated emission of characteristic X-rays of the inner shell electrons of the elements that make up the sample. Techniques used to displace the inner shell electrons and induce the X-ray emission include bombardment of the sample with high intensity, narrow-band radiation from X-ray or gamma ray sources or with high-energy particles such as electrons or neutrons. The characteristic X-rays that are emitted are measured using one of two techniques: the older wavelength-dispersive method or the more recent energy-dispersive method.

69. In both methods, the secondary X-rays from either solids or solutions are excited by using a high-intensity beam of primary X-rays. In the wavelength-dispersive method, the emitted X-rays are columnated and dispersed by reflection from a crystal so that a typical X-ray spectrum is produced, the peaks and peak-heights are indicative of what atoms and how many each are present. The emission spectrum is complex and depends upon the X-ray source (the target in the primary roentgen tube) and the absorption (interferences) and enhancement (secondary fluorescence from matrix elements exciting the analyte atoms) characteristics of the sample.

70. The energy-dispersive method depends upon a lithium-doped silicon detector that produces a pulse from individual quantum absorption events proportional to the energy in the quantum. The pulses are collected and processed in a multichannel analyzer. The primary advantage of the technique is that a true simultaneous multielement analysis is accomplished. A major disadvantage is the method's lack of high resolution; the best typical resolution is about 150 eV (compared with about 3 eV in the wavelength-dispersive method), which means that serious overlap occurs between lines for neighbors in the periodic table.

71. A technique is sometimes employed in which X-ray fluorescence is induced by bombarding the sample with a beam of protons accelerated to 3 to 5 MeV--proton-induced X-ray emission analysis, or PIXIE. Very low detection limits can be attained with this method because of the high energy of the excitation beam, but the lack of a particle accelerator in most laboratories precludes its use under routine circumstances. Table 8 compares detection limits for these three XRF methodologies.

Neutron Activation Analysis (NAA)

72. NAA is based upon the principle of the conversion of stable isotopes of elements of interest to radioactive isotopes by bombarding the stable isotopes with high-energy neutrons and then measuring the magnitude of the

Table 8
Comparison of Typical Detection Limits for Selected
X-Ray Fluorescence Techniques, ng/cm² • 100 sec

<u>Element</u>	<u>Wavelength- Dispersive</u>	<u>Energy- Dispersive</u>	<u>Proton- Induced</u>
As	5.8	1.6	0.5
Ba	0.8	25*	-
Cd	2	3.6	14
Fe	12	5.3	0.13
Pb	32	4.5	2.5
Zn	2	3.3	0.25

resulting radioactive decay process. NAA methods are potentially the most sensitive of any of the techniques that are available to the trace metal analyst. Unfortunately, their advantages are offset by the high cost of acquiring and maintaining a reactor for irradiation, the difficulty of performing the necessary separations to ensure accuracy, and the length of time performing the necessary separations to ensure accuracy at the trace level (1 hr to irradiate and up to 30 days to detect).

Mass Spectrophotometry (MS)

73. In MS, the sample is vaporized in the vicinity of an ionizing field and accelerated through a magnetic field that separates the ions according to their mass-to-charge ratio. The abundance of the separated ions is proportional to the amount of analyte present in the original sample. The mass spectrum represents the total composition of the sample. Most commercial mass spectrometers have sufficient resolution and dynamic range to allow the detection of essentially each isotope of every element in the periodic table. The main types of mass spectrometry that have application in trace metal analysis are electron bombardment of organic-metal complexes, thermal ionization of inorganic salts, and spark source ionization of solution residues.

74. Sciex Company (1986) has combined an ICP with MS to produce an instrument capable of multielemental analysis with detection limits for most elements in the 0.01- to 1-ppb range. It can determine up to 30 elements/min for any particular sequence of elements and has a dynamic range of at least five orders of magnitude. It is also useful for isotope studies such as isotope dilution. The ICP serves as an ion source for the MS.

Voltammetric Methods

75. Voltammetry involves different methods of measurement of an oxidation-reduction process as a function of an applied voltage. A voltammogram is obtained by recording the current as the applied potential is continuously changed. Inflection points or peaks in the voltammogram represent the oxidation or reduction of a specific species in the sample solution. This is one of the few analytical techniques that provides direct information about the oxidation state, speciation, and degree of complexation of a specific

analyte as indicated by the analyte redox potential while the measured current is proportional to the analyte concentration.

Polarography

76. Polarography, the classical voltammetric technique, uses a cell that has three electrodes: working, reference, and counter electrodes. The working electrode consists of a continuously dropping mercury stream that provides a constantly renewed electrode surface. A polarogram is obtained by slowly changing the DC applied potential from -0.3 V versus the saturated-calomel reference electrode (SCE) to about -2.0 V versus SCE. The diffusion current from the oxidation-reduction process is measured as a function of this varying voltage. Concentrations of analyte species are obtained by comparison of diffusion currents obtained with the unknown with those obtained with standard solutions. Electroactive species at millimolar to micromolar concentrations can be detected by conventional DC polarography.

Pulse polarography

77. Basically the same as conventional DC polarography, the increase in voltage is applied to each mercury drop from the mercury working electrode. The primary advantage to this technique is that when the faradic current is measured near the end of the drop life-time, the background capacitance current is nearly zero. This increases the sensitivity to about $0.1 \mu\text{mol}$ and increases the resolution. In the differential pulse method, pulses of constant amplitude are superimposed upon a continuously increasing DC voltage ramp. Since the difference in voltage between two subsequent voltage pulses is what is measured, the output is the derivative so that peaks rather than waves are recorded, giving much better resolution between successive peaks. Reliable separation can be resolved with concentration differences between the two analytes as high as 10,000 and redox potentials differing by a few millivolts.

Stripping voltammetry

78. In anodic stripping voltammetry, a stationary electrode (either a hanging mercury drop or rotating thin film) is stirred rapidly in the sample solution to reduce the metals and to form a mercury amalgam. This effectively preconcentrates the metals in the sample onto the electrode by a factor of 100 to 1,000. Subsequent oxidation of the reduced species on the electrode by a scanning voltage (either DC, pulse, or differential pulse) and measurement of the resulting current quantify the analyte concentration in the sample.

Typical detection limits on the order of nanomolar or less are feasible. Some typical detection limits are illustrated in Table 9. Stripping analysis of trace metals in a variety of substrates is reviewed by Wang (1985).

Multielement analysis using a combination of voltammetric methods

79. The determination of up to eight elements (As, Cd, Co, Pb, Cu, Ni, Se, and Zn) at major, minor, trace, or ultratrace levels using a simple and reliable multielement approach has been reported by Adeloju, Bond, and Briggs (1985). By using a dropping mercury electrode, a combination of methods (including differential pulse polarography, anodic and cathodic stripping voltammetry, and absorption voltammetry) can be applied to a single sample of solution. The methods used depend upon the constituents being analyzed and their concentrations. The determination of eight elements in the digested sample takes about 3 hr, or approximately 25 min/element/sample.

80. A new generation of polarographic analyzers is on the market with varying potential for semiautomatic or fully automatic operation: EG & G Princeton Applied Research Corporation (Model PAR-384B), Bioanalytical Systems, Inc. (BAS-100), and Metrohm A.G. (646-VA). With microprocessor control, they can be programmed for routine addition of reagents and standards.

Ion Chromatography

81. Chromatography is one of the most effective known methods of separating interfering constituents prior to analysis. Most chromatographic separations of mixtures are routinely accomplished in a few minutes with relatively simple and inexpensive equipment. By using the high selectivity of a

Table 9
Typical Detection Limits for Anodic Stripping Voltammetry*

<u>Element</u>	<u>Differential Pulse</u>	<u>Linear Scan</u>
Cd	0.005	0.01
Cu	0.005	0.01
Pb	0.01	0.02
Zn	0.04	0.04

* All analyses are made with metal thin film electrode with 2-min deposition. All measurements are in mg/l (ppm).

chosen chromatographic separation, a relatively simple and nonspecific method of detection can be used to effect a highly sensitive, specific, and precise analysis of sample constituents.

82. Chromatography includes a variety of processes that incorporate a common principle: the differential distribution of sample components between two phases. The stationary phase remains fixed in the system whereas the mobile phase flows through or over the surface of the fixed phase. This movement of the mobile phase effects a differential migration of the sample components, based upon several phenomena including differential solubility, adsorption, molecular size, and complexation. Types of chromatography are classified based upon the types of phases that are used, the mobile phase being named first: gas-liquid, gas-solid, liquid-liquid, and liquid-solid.

83. Ion chromatography (IC) is a special case of liquid-solid chromatography applicable to both organic and inorganic species that are ionic in nature. A simple IC system applicable to metal ions is diagrammed in Figure 1. This system effects separation of cations on a strong acid cation exchanger using HCl as eluant. Although separation of the metals occurs in the "separator column," the high level of chloride ions produces a large background signal that prevents sensitive conductivity detection of the low levels of metals. Passage through a second column, the "suppressor column," exchanges the chloride ions for hydrogen ions on a strong base anion exchanger in H⁺ form so that only the metals are detected by the conductivity detector on a background of deionized water. Suppression of the high chloride background greatly increases the sensitivity of the system to the lower concentration of metal ions in the sample. With the latest developments in high-efficiency separator columns and high-capacity suppressor columns, the routine determination of common alkali and alkaline earth metals along with ammonium in a single injection run less than 15 min (Rubin and Heberling 1987).

84. Two types of detectors are in common use: conductivity detectors and indirect photometric detectors (Small 1981, Mulik and Sawicki 1979). Conductivity detectors require the removal of the high level of the eluant ions by the use of a "suppressor" column before the detector. Conductivity detectors have the advantages that they can easily be miniaturized and are sensitive to all ionic species often in the parts-per-billion range; however, they also show a high sensitivity to temperature and require suppression of all other ions. The suppressor column with conductivity detection is not

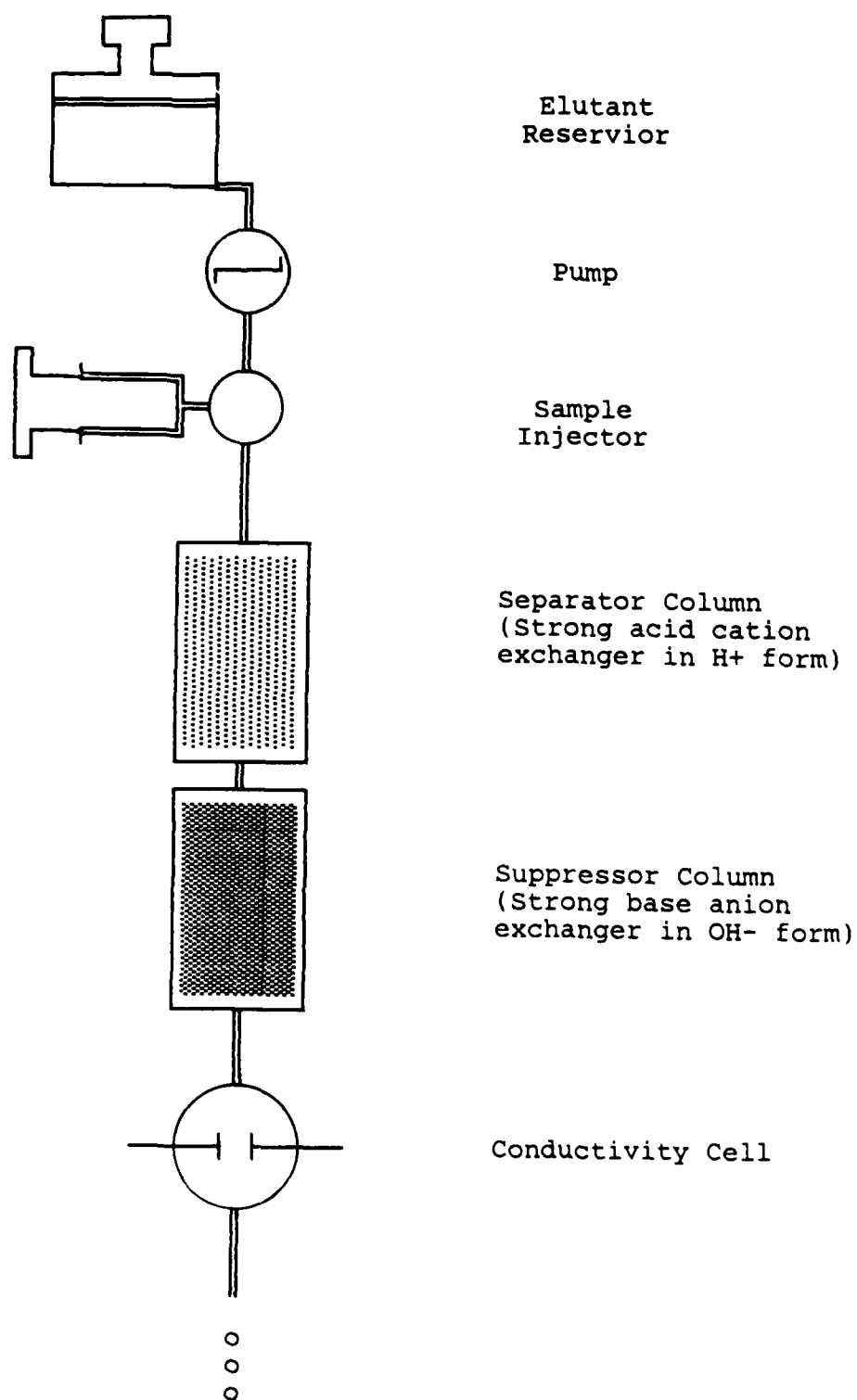


Figure 1. A simple system for cation analysis by ion chromatography with conductivity detection

usable with transition metal ions because they precipitate as hydroxides in the suppressor column before entering the detector, or with tightly-bound, sample ions that mask conductivity detection. A recent method to overcome this problem of metal precipitation employs prederivatization of the metal ions as stable, anionic, metal complexes. For example, by using EDTA as eluant, prederivatized complexes of several trace metals have been separated and detected in a single determination using a suppression column and a conductivity detector (Pohl, Haak, and Fitchett 1984); metal complexes successfully determined from a single injection were Pb (EDTA)^{2-} , Cu (EDTA)^{2-} , Zn (EDTA)^{2-} , Ni (EDTA)^{2-} , and Cr (EDTA)^{2-} . Stable cyanide-metal complexes have also been shown amenable to this procedure (Fitchett, Johnson, and Pohl 1983) as Au(CN)_2^- , Au(CN)_4^- , Ag(CN)_2^- , and Co(CN)_6^{3-} . This method was proposed as especially applicable to cyanide containing plating solutions. Other anion metal complexes have been suggested. However, as these procedures require a prederivatization step with its inherent problems, they are not widely used for trace metal analyses at this time.

85. Photometric detectors, which were announced in 1982 (Small and Miller 1982) and have recently been patented (Small and Miller 1983), have found recent commercial application (Dionex Corporation 1985, MacBlane and Benson 1985, Rubin and Heberling 1987). For metals, photometric detection comprises a postcolumn reactor (instead of the suppressor column) that visualizes the metal bands by combining a coloring reagent with the eluant stream. This method can determine a wide variety of metals at very low concentrations without prederivatization. Liquid samples are introduced to the separator column using typical IC techniques and eluants. Metal bands migrate through the column at rates determined by their affinity to complex with a ligand added to the eluant versus their electrostatic affinity for the stationary ion exchange sites. After passing through the column, the effluent is mixed with a strong, metal-complexing, colorimetric reagent. The metal bands can then be detected at visible wavelengths in a flow-through cell absorbance detector. The postcolumn reagent most widely used to visualize the metal ions for spectrometric determination is 4-(2-pyridylazo) resorcinol, which forms a colored complex (absorbing strongly between 520 and 540 nm) with wide variety of transition and posttransition metals (Heberling and Riviello 1985). Up to 10 metal ions have been determined in a single injection using an improved Dionex HPIC-CS5 column with pyridine-2,6-dicarboxylic acid as eluant.

86. In typical chromatographic procedures, each metal in the sample is identified and quantified by comparing the chromatogram with those made with standard solutions. Because only metal ions of interest are detected, ion chromatography is often less subject to interferences compared with other methods. By selecting the appropriate column for separating the ions of interest in a sample, analysts can now separate and analyze the oxidation state of many metals and can determine Group I and II metals, metal complexes, and a complete range of inorganic and organic ions in a sample with excellent speed (usually less than 20 min/sample) and sensitivity. Typical detection limits, as compared with flame AA, are given in Table 10 for direct injection and for preconcentrated samples of ideal, single components in deionized water. Notice the small injection volumes (50 μ l). Sample preconcentration can be performed within the system and does not require additional sample handling. Ion chromatography is becoming an important complement to diversify the elemental capabilities of laboratories employing only AA or ICP instrumentation (Rubin and Heberling 1987).

Table 10
Typical Metal Detection Limits by Ion Chromatography*

<u>Metal</u>	<u>Species Detected</u>	<u>Minimum Detection Limit, ng/ml</u>		
		<u>Direct**</u>	<u>Preconcentrated**</u>	<u>Flame-AA</u>
Ba	Ba(2+)	100	0.1	20
Cd	Cd(2+)	10	0.1	1
Cr	Cr(III)	1,000	10	3 †
	(as CrEDTA ⁻)			
	Cr(VI)	50	1	3 †
	(as CrO ₄ ⁻)			
Cu	Cu(2+)	5	0.05	2
Fe	Fe(II)	10	0.1	5 †
	Fe(III)	3	0.03	5 †
Pb	Pb(2+)	100	1	1
Ni	Ni(2+)	25	0.3	8
Ag	as Ag(CN) ₂ ⁻	100	10	2
Zn	Zn(2+)	10	0.1	0.6

* Adapted from Dionex Corporation (1985).

** Direct injection using a 50-μl sample loop.

Preconcentrated refers to 5 ml of sample preconcentrated, then injected.

† Where two oxidation states can be determined by IC, AA can detect only the total metal; this is the detection limit shown.

PART III: SAMPLE PREPARATION AND ENRICHMENT

Introduction

87. Seldom can the concentrations of trace heavy metals in natural water or waste sludge samples be determined by any analytical procedure without some preanalysis chemical treatment. The need for sample work-up prior to chemical analysis has not been diminished by recent instrumental developments. Samples to be analyzed for trace metals by molecular spectrometry or ion chromatography are generally introduced into the spectrometer or chromatograph as liquids. The care and attention given to the final instrumental analysis are of little value unless the sample remains representative and is not altered during preparation. Preanalysis chemistry is as important to the overall accuracy and precision of the process as the actual analytical methodology itself.

88. This part deals with developments in sample pretreatment that increase the reliability of the data, the detection limits of the trace elements, and/or the overall value of the final results to the objectives of the analytical program. Preanalysis manipulation primarily concerns getting the samples into a form compatible with the analytical technique being used; this includes filtration, solubilization, and removal of interfering matrices. A further concern is the separation of the sample into constituent phases and chemical and/or physical categories (speciation) so that the distribution and environmental effects of the analytes can be better understood. Several recent reviews cover many of these topics in detail (Minczewski, Chwastowska, and Dybczynski 1982; Mizuike 1983).

89. Major concerns are the presence of particulates in the sample and ways to handle them. While low levels of solids can be accommodated by some equipment, the uncertainty as to whether the solids are atomized makes results produced in their presence uncertain. Filtering the sample is a potentially serious source of error as the sample contacts large solid areas where significant losses can occur as well as contamination from the filter media. Within limitations, centrifugation can also be used for particulate removal. If total analyte concentration in the sample is desired, the particles can be reduced, oxidized, or digested to soluble forms before analysis. Some particulates may consist of colloidal, nonpolar micelles. Natural or introduced

hydrocarbon fractions can be separated from the aqueous phase by solvent extraction. Baudo, Galanti, and Varini (1983) have enumerated nine analytical errors associated with two procedures for determining the trace element content of fresh/water particulate matter by AAS. The precision and accuracy of two methods -- removal of particles from filters by ultrasound or destroying filter by ashing -- were compared. The effects of pH on the effectiveness of metal removal from sediments and suspended particulates were assessed by Trefry and Metz (1984). The fraction of metal removed by phthalate buffers varied with sample composition, final pH, and the element determined. The effects of equilibration time, aqueous/solid ratio, solution matrix, wet versus dry sample, and final pH on the technique were evaluated.

Decomposition and Solubilization Techniques

90. For those samples containing a solid phase, such as most waste waters, tissue samples, sediments, and sludges, dissolution is the typical first step in analysis. Among the more common decomposition methods are digestion with acids and combustion with oxygen or appropriate fluxes. The former is subject to contamination by impurities in the reagents, whereas the latter may lose volatile components and/or introduce contamination if fluxes are used. Typical decomposition techniques used in inorganic trace analysis are listed in Table 11. A universal decomposition method that is adequate for samples does not exist (Tatro 1985).

Acid digestion and wet oxidation

91. Acid digestion under oxydizing conditions is a common first step in analytical procedures for trace metals. This procedure dissolves suspended materials, converts dissolved organics to carbon dioxide and water, and defines the anionic medium for matrix matching. Acids used to dissolve sample matrices are shown in Table 12. Appendix C provides specific information on various digestion techniques. Basic digestion techniques have been detailed in many sources (USEPA 1983, ASTM 1985). The USEPA (1983) recommends heating with serial additions of concentrated nitric acid and a final addition of HCl. The ASTM (1985) recommends a milder treatment using concentrated HCl. Hydrofluoric acid may be necessary to digest some siliceous particulates if a total digestion is to be accomplished.

Table 11
Decomposition Techniques Used in Inorganic Trace Analysis

For inorganic solids:

Dissolution in mineral acids, organic acids, or alkali hydroxide solutions, etc.

Fusion or sintering with alkali carbonates and hydroxides, sodium peroxide, alkali disulfates, etc.

Decomposition with reactive gases such as oxygen, chlorine, and hydrogen fluoride.

Anodic dissolution (electrolytic dissolution).

For organic samples:

Dry oxidation (dry ashing) in air, oxygen, or oxygen plasmas.

Wet oxidation (wet ashing) with mineral acids.

Oxidative fusion with alkali nitrates.

92. For liquid waste samples, the USEPA (1977) has recommended a nitric acid-hydrogen peroxide digestion procedure for trace metal analysis. A similar methodology (USEPA 1979a) has been recommended for the solubilization of sewage sludge prior to elemental analysis. In the latter method, the sample is taken to dryness and refluxed with 1:1 nitric acid and hydrogen peroxide; the last refluxing includes addition of HCl for furnace analysis of some metals (Sb, Be, Cd, Cr, Cu, Pb, Ni, and Zn) or the addition of nitric acid for some others. The USEPA (1982) proposed several additional and modified decomposition techniques. These later techniques do not take the sample to dryness and usually recommend keeping the temperature below boiling.

93. A steam digestion method for metal (Cd, Cr, Cu, Ni, and Zn) determinations in sewage and sludge is described and compared with methods using nitric acid digestion and high-speed homogenization by Nielsen and Hurdey (1984). Twenty-millilitre, acidified (1-percent v/v nitric acid) aliquots of raw sewage, mixed liquor, primary sludge, and reference sludge samples were placed in 50-ml pyrex test tubes and digested for 1 hr at 210 kPa (2 atm) in a domestic pressure cooker. The method gave quantitative metal recoveries and was less prone to contamination than open nitric acid digestion or high-speed homogenization methods.

Table 12
Acids Used To Dissolve Inorganic Solids*

Acid	Common Uses
HCl	For many salts of weak acids: carbonates, phosphates, some oxides (e.g., Fe_2O_3), some sulfides. At high temperatures (250 to 300° C) in a sealed tube, HCl dissolves strongly ignited Al_2O_3 , BeO, SnO_2 , and some silicates. At 350 to 400° C with HClO_4 or other oxidizing agent, dissolves Rh, Ir, Os, and Ru.
H_2SO_4	Used when its high boiling point (300° C) is an advantage, as in expelling a volatile product or increasing reaction rate (e.g., for decomposing CaF_2 and monazite (phosphate of rare earths and thorium)). Advantageous for formation of sulfate complexes and dehydrating and oxidizing properties at high temperatures.
HNO_3	Provides oxidizing attack for metals not dissolved by HCl and other nonoxidizing acids. Au, Pt metals (except Pd), Nb, Ta, and Zr not dissolved. Al and Cr are passivated. Sn, Sb, and W give insoluble hydrous oxides. Dissolves most sulfides (except HgS). Usually not appropriate for oxides (except UO_2 and U_3O_8).
HClO_4	At fuming temperature, a strong oxidizing agent that destroys organic matter. Therefore, mix with HNO_3 to oxidize easily attacked organic matter that might otherwise react violently with HClO_4 . H_2SO_4 (dehydrating agent) increases oxidizing power. Good solvent for stainless steel, sulfides; with H_3PO_4 dissolves chromite (FeOCr_2O_3). Does not dissolve Pt metals (except Pb), Nb, Ta, or Zr.
HF	For decomposition of many silicates in combination with H_2SO_4 or HClO_4 to eliminate fluorides. With HNO_3 , dissolves Ti, W, Nb, and Zr (also their carbides, nitrides, and borides) as a result of formation of complex fluorides. Certain refractory silicates and other minerals not decomposed; these must be dissolved by fusion.

* Adapted from Sotera and Kahn (1982).

94. Various digestion procedures for soils and sewage sludges for AAS analysis were compared by Berrow and Stein (1983). Refluxing with aqua regia was more effective than digestion in an open vessel and produced results comparable with those obtained by bomb digestion (see following paragraphs), which was the most vigorous method used. Over 90 percent of total Cr, Cu, Pb, and Mn was extracted from sewage sludges and sludge-treated soils. Sinex,

Cantillo, and Helz (1980) have also compared acid extraction methods with sediments for trace metals.

95. Samples of wastewater and other environmental samples were decomposed with a mixture of sulfuric acid and hydrogen peroxide before Se reduction for hydride-generation AAS (Krivan et al. 1985). Radiotracer error diagnosis showed recoveries of 99.7 percent in the decomposition step, 98 percent in reduction, and 95 percent in hydration.

High-pressure acid or
hydrogen peroxide decomposition

96. Several high-pressure decomposition vessels have been introduced commercially; Parr Instruments Company, Perkin-Elmer Corporation and the Uni Seal Decomposition Vessels, Ltd., all make Teflon-lined, steel cylinders that are designed to hermetically seal the digestion mixture at elevated temperatures and pressures. Advantages of these Teflon decomposition bombs over wet digestion are (a) faster digestion, (b) high efficiency of destruction under pressure, (c) virtual elimination of losses of volatile elements, and (d) relatively small quantities of mineral acid requiring a reduction of contamination from the reagents.

97. Typically for the use of digestion "bombs," 0.25 to 0.5 g of dry sample is weighed into the Teflon container and treated with 2.5 to 5 ml of redistilled nitric acid. The container is sealed into its steel cylinder, and the assembly placed at 100° C (or autoclave) for a few hours or overnight. Complete digestion of difficult samples can often be accomplished using such equipment (see DeAntonio et al. 1981, Katz et al. 1981). Okamoto and Fuwa (1984) describe a double-walled, digestion bomb for low-contamination digestion of complex organic matrices.

98. Dried wood samples were decomposed in a bomb made of Teflon with 50-percent hydrogen peroxide heated in an oven at 125° C for 4 hr (Matusiewicz and Barnes 1985). The digestion permitted the use of aqueous standards and minimized any potential matrix effects. Twenty-one element concentrations were obtained sequentially by electrothermal vaporization ICP-AES using 5- μ l sample aliquots.

99. Three methods of decomposition of marine biological tissues for analysis of the volatile metals, As, Hg, and Se, by hydride-generation and cold-vapor AAS were compared by Welz and Melcher (1985). Decomposition with nitric acid under pressure in a PTFE bomb resulted in low values for As and Se

but was adequate for the subsequent determination of Hg; decomposition with nitric, sulfuric, and perchloric acids gave the highest values for As and Se, but Hg was partly lost; combustion in a stream of oxygen gave results with all three. Welz and Melcher (1985) recommend pressure decomposition with nitric acid for Hg followed by a sulfuric and perchloric acids treatment for As and Se.

Microwave digestion

100. Microwave oven dissolution of samples has been proposed as an alternative to "bomb" digestion (Matthes, Farrell, and Mackie 1983; Nadkarni 1984; Tatro 1985). Microwave heating in the presence of strong acids dissolves the metals from powdered coal, fly ash, oil shales, rocks, sediments, and biological samples within 3 min, thus saving at least 2 hr/sample (Nadkarni 1984). Metals in nonporous organic solids such as heavy oils or coke are not effectively removed by the method. Nearly 25 elements, including As, Be, Ba, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, have been successfully analyzed from a variety of matrices by microwave digestion followed by ICP-AAS. Papp and Fischer (1987) found microwave digestion of peat for AAS determination of metals (Ca, Mg, Fe, Al, Mn, Zn, Cu, and Li) agreed well with a dry ashing method and a nitric-perchloric-hydrofluoric acid wet digestion with the advantages of only taking 2 hr and using less acid, which minimizes contamination and leads to lower blank values.

101. A commercial microwave digestion system designed especially for trace metal sample preparation has been announced by CEM Corporation (Model #MDS 81D). Initial studies using the system were presented by Jassie and Kingston (1985). An operator's manual being developed will detail microwave power settings and corresponding pressure and temperature profiles for various types of samples and acids. The system features PFA-closed vessels that will tolerate up to 100 psi, a Teflon-lined cavity that reduces metal contamination, and a turntable that reduces hot spots during the digestion.

Dry ashing and fusion techniques

102. Sample matrices containing appreciable levels of organic or inorganic solids are often more easily solubilized after dry ashing or fusion with a variety of ashing aids and fluxes. Ashing techniques are described in Appendix D. The residues are then dissolved in appropriate solvents for introduction into the analytic system. Water or wastewater samples are not usually prepared using these techniques.

103. Sewage sludge samples have been prepared for atomic absorption spectrometry by dry ashing (Ritter et al. 1978, Bergman et al. 1979). One-gram samples in acid-washed, porcelain crucibles were ignited at 500° to 550° C for 150 min in a muffle furnace. Twenty-five millilitres of 3 N HCl was added to the ashed samples after they had cooled in 50-ml Folin-Wu tubes. The samples were heated to 120° C for 2 hr, filtered through Whatman #42 paper, and diluted to final volume. These procedures were effective for a variety of sewage sludge samples.

104. Fusion techniques are typically used for siliceous samples such as soils and sediments. Common fusion reagents are listed in Table 13. Early reports fused the samples with lithium metaborate at high temperature followed with nitric acid dissolution of the residue (Brown and Newman 1973). For example 0.2- to 0.5-g samples of sewage sludge have been fused with 2-g lithium metaborate by heating for 15 min at 900° C (Van Loon and Parissis 1969). Sinex, Cantillo, Helz (1980) compared lithium metaborate fusion with acid digestion for trace metals in sediments. Fusion techniques gave generally higher values. Sodium peroxide fusion has been used for lake sediments or other geological materials (Nadkarni and Morrison 1978, Van Loon 1980). Geological samples have been fused with potassium pyrosulphate, and the fusate has been dissolved in a solution of hydrochloric acid, ascorbic acid, and potassium iodide (Viets, O'Leary, and Clark 1984). This solution is solvent extracted, giving determination of Ag and Cd down to 0.1 ppm; Cu, Mo, and Zn to 0.5 ppm; Pb to 1 ppm; and As to 5 ppm.

105. The low-temperature oxygen plasma asher can be quite useful for samples principally containing suspended organic matter or for animal or plant tissues. Oxygen radicals, produced by radio-frequency discharge, destroy the organic matrix of the samples. Human liver samples have been ashed at temperatures well below 100° C, but 14 g of fresh liver required 60 hr to be ashed (Locke 1979). Recoveries compared favorably with those obtained by conventional wet digestion and dry ashing procedures for Ca, Cd, Cu, Fe, Mg, Mn, and Zn. Earlier work had cited good recoveries for most metals using this technique but found some losses of Ag and Hg from blood samples (Zief and Mitchell 1976).

Table 13
Common Fusion Reagents*

Reagent	Comments
Sodium hydroxide	Seldom used. 500 ^o C. Attacks platinum and porcelain. Use nickel or graphite crucible. Dissolve residue with 12 M hydrochloric acid.
Sodium carbonate	Classical technique. 800 ^o C. Dissolve with hydrochloric acid.
Lithium metaborate	Widely used. 900 to 1,000 ^o C. Dissolve with hydrofluoric acid.
Lithium tetraborate	Widely used. 900 to 1,000 ^o C. Dissolve with hydrofluoric acid.
Potassium hydroxide	Seldom used. 500 ^o C. Use nickel or graphite crucible. Dissolve residue with 12 M hydrochloric acid.
Potassium persulfate	Very useful, dissolves practically everything. 900 ^o C. Dissolve with sulfuric acid.

* Adapted from Sotera and Kahn (1982).

Concentration and Enrichment Techniques

106. Water and wastewater samples, or those produced from solubilized solid samples, often require further treatment either to raise the level of analytes to their optimum for analysis (concentration) or to lower levels of interfering materials or differentiate between ionic or complexed species in the sample (separation/speciation). These techniques are often considered simply as enrichment, typical techniques for which are listed in Table 14. Some unique combinations of gas and liquid chromatography with atomic spectroscopy have been reported to give a high degree of selectivity and enrichment of selected analytes in complex matrices (Ebdon, Hill, and Ward 1986 and 1987), but these methodologies are not generally applicable for day-to-day operations.

107. USEPA has made an exhaustive study of seven of the most promising preconcentration techniques for USEPA's inorganic priority pollutants (Leyden 1983). They concluded that the most effective methods were those based upon the addition of precipitating reagents containing the dithiocarbamate group. These reagents react with a broad scope of ions and are relatively insensitive

Table 14
Enrichment Techniques Commonly Used in Inorganic Trace Analysis

Solid or molten samples

- | | |
|--------------|--|
| Particles* | + Manual selection under the microscope. Sieving. Magnetic separation. Heavy liquid separation. Flotation. |
| Constituents | + Selective Dissolution. Electrolytic dissolution. Sublimation. Extraction of gasses in metals at high temperatures. Dry oxidation of organic samples. Zone melting. Fire assay. |

Solutions

- | | |
|------------|---|
| Particles* | + Filtration. Centrifugation. Flotation. |
| Solutes | + Precipitation. Electrodissolution. Adsorption. Molecular sieving. Ion exchange. Liquid-liquid extraction. Volatilization. Flotation. Freezing. Electrophoresis. Dialysis. Ultrafiltration. Ultracentrifugation. |

Gas

- | | |
|--------------|---|
| Particles* | + Filtration. Impaction. Sedimentation. Centrifugation. Thermal precipitation. Electrostatic precipitation. |
| Constituents | + Absorption. Adsorption. Condensation. Permeation. |
-

* Particle diameter > ca. 0.5 μm .

to the presence of organic materials. This publication is recommended for a good discussion of various preconcentration methodologies.

108. Trace recovery (R_t), or the yield of the desired trace element, is defined as:

$$R_t = \frac{Q}{Q^0} \times 100(\%) \quad (1)$$

where Q^0 and Q are the quantities of the desired trace element before and after the enrichment, respectively, the latter being corrected for contaminants. The trace recovery is usually less than 100 percent because loss of the desired trace element may occur during the decomposition and enrichment steps by evaporation, incomplete decomposition, incomplete separation,

careless manipulation, and adsorption on the walls of containers and other apparatus used. In general, the lower the concentration, the more the danger of losses. The well-known anomalous behavior of trace metals at extremely low concentrations is frequently responsible for the loss. Trace recoveries of greater than 95 percent, or 90 percent at least, are required in most inorganic trace analyses. If sufficiently reproducible, lower trace recoveries can be used for the correction of analytical results. Standard samples, i.e., certified standards, analyzed samples or synthetic samples, are used for determining trace recoveries. Recoveries of over 100 percent are indications that contamination is occurring.

109. The enrichment factor (F), or preconcentration coefficient, of the trace element is defined as:

$$F = \frac{\frac{Q}{M}}{\frac{Q_o}{M_o}} = \frac{R_t}{R_m} \quad (2)$$

where M_o and M are the quantities of the matrix before and after the enrichment respectively and R_m is the yield of the matrix.

Solvent extraction

110. Solvent extraction is often the method of choice because of its simplicity, speed, and wide application. Most extractions take only a few minutes, employ simple apparatus such as a separatory funnel, and can be used for both trace and macro analyses. Since most metal salts are only slightly soluble in organic solvents, their extraction from aqueous media requires masking the ionic charges and replacement of hydrating water molecules by other coordinating groups. Recent reviews cover techniques for extraction of metal ions from aqueous solutions into immiscible organic solvents (Kraak 1983).

111. The most common extraction schemes involve the use of the formation of metal chelates. The Lewis acidity of the metal ion, the Lewis basicity of the polydentate ligand, and the pH of the aqueous solution are the primary factors in the formation of the metal chelates. In the general case, metal chelate concentration $[ML_2]$ follows from the model:

$$[ML_2] = K_f [M^{++}] [L^-]^2 \quad (3)$$

where $[L^-]$ is the concentration of the polydentate ligand that is the conjugate base of the weak acid, HL, and its concentration depends upon the K_a of the acid and the pH of the system. $[M^{++}]$ is the free metal ion concentration.

112. A commonly used metal chelator, pyrrolidine dithiocarbamic acid (or its ammonium salt, ammonium pyrrolidine dithiocarbamate (APDC)), reacts with the majority of heavy metals. Table 15 details the ranges for their formation and extraction.

113. The extraction of the metal chelate, ML_2 , depends upon its relative solubility in the extracting organic phase and in the initial aqueous phase. Characteristics of the solvent necessary for efficient extraction include: immiscibility with the aqueous phase, high solvency for the metal chelate, and compatibility with the analytical technique. Methyl isobutyl ketone (MIBK) is most commonly used as an extracting solvent and meets these requirements quite well routinely allowing 10-fold concentrations when coupled with APDC-metal chelates.

114. Procedures required by the USEPA (1982) using APDC as chelator and MIBK as extraction solvent are published in "Test Methods for Evaluating Solid Waste: Physical/Chemical Methods." This procedure frequently increases sensitivity in AAS by 30 to 40 times. The USEPA recommends this procedure when the concentration of the metal is not high enough to determine directly or when considerable dissolved solids are present in the sample. They suggest that the procedure is particularly useful for Zn, Cd, Fe, Mn, Cu, Ag, Pb, and Cr(VI). Cr(III), Al, Be, Ba, and Sr do not react with APDC.

115. Backstrom, Dnielsson, and Nord (1984) devised a continuous flow extraction process incorporating a flow injection system on a graphite furnace AAS. This analysis system cannot use MIBK as an extractant because of its water solubility and the volatility of the carbamate complexes. Instead, they released the metal from the extracted APDC complex with Hg, which forms stronger complexes with dithiocarbamates, so that the metals can be transferred back to an aqueous solution. They concentrated 0.1-ppm concentrations of Cd, Cu, Fe, Pb, Ni, and Zn in 0.7-M Na from 25- to 30-fold without serious losses (mean extraction yields from 86 to 108 percent) and without Na pass-through.

Table 15
Typical pH Ranges for the Formation of Metal-APDC*
Chelates and Their Extraction into MIBK** †

<u>Metal ion</u>	<u>Formation Range</u>	<u>Extraction Range</u>
Arsenic (III)	0 to 6	2 to 4
Cadmium (II)	0 to 14	1 to 10
Chromium (?)	2 to 9	3 to 7
Copper (II)	0 to 14	1 to 10
Iron (II)	2 to 14	--
Iron (III)	2 to 14	2 to 5
Lead (II)	0 to 14	1 to 10
Manganese (II)	2 to 14	5 to 10
Mercury (II)	0 to 14	0 to 10
Nickel (II)	1 to 14	1 to 10
Selenium (?)	2 to 10	3 to 6
Silver (I)	0 to 14	0 to 14
Zinc (II)	2 to 14	1 to 10

* APDC = Ammonium pyrrolidine dithiocarbamate.

** MIBK = Methyl isobutyl ketone.

† Adapted from Parker (1976).

116. Aliquat-336 (quaternary ammonium salt, tricaprylmethylammonium chloride) has been shown to be a versatile extractant for metals that are capable of existing as complex anionic species (Grudpan and Taylor 1984). It has been used for concentrating Cd from aqueous solutions containing ppb levels and for Cr, Mo, Au, and Co. Aliquat-336 and MIBK have also been used successfully to extract As, Ag, Cd, Cu, Pb, and Zn from geological samples that have previously been fused with potassium pyrosulfate (Viets, O'Leary, and Clark 1984).

117. Beta-diketonate complexes of Fe, Cu, Zn, Mn, Al, and Cr in xylene were directly introduced by pneumatic nebulization into an ICP-AES (Black, Thomas, and Browner 1981). Operating parameters are discussed and detection limits given also for the metals as their trifluoroacetylacetonate complexes in xylene as compared with those obtained with aqueous solutions.

118. When two elements form extractable chelates with a particular chelating agent, a large difference in the pH values where the distribution ratio is unity for both elements is required to achieve successful mutual separation at an appropriate pH. By adding masking agents, the pH values

where the distribution ratio is unity can be shifted so that the two elements can be effectively separated. Common masking agents include cyanide, tartrate, citrate, fluoride, and ethylenediaminetetraacetic acid (EDTA). These agents prevent the extraction of metal elements into the organic phase by forming strong water-soluble (usually negatively charged) complexes. The selectivity in chelate extraction systems can be improved by simultaneously using two or more masking agents. A large number of elements are extracted into chloroform or carbon tetrachloride with dithizone (diphenylthiocarbazone), but use of masking agents and adjustment of pH of the aqueous phase restrict the number of extracted elements. See Mizuike (1983) for a complete, theoretical discussion of masking and its uses. King and Fritz (1985) describe a selective extraction technique for dilute heavy metals using bis(2-hydroxyethyl) dithiocarbamate to form neutral metal complexes. Selectivity is accomplished by masking agents and pH adjustment and sorption on a small XAD-4 resin column.

Evaporation of solvent

119. Evaporation of solvent is often the concentration method of choice for analysis of very dilute samples of nonvolatile trace metals. The procedure is simple, and large relative concentration factors (100 to 500) can easily be obtained if adequate precautions are made to reduce contamination. This simple and obvious procedure suffers two major disadvantages: first, if the original sample contained interfering, or potentially interfering, elements or high total dissolved solids (TDS), both will be concentrated to the same extent as the analytes; and second, losses in analytes may occur as the result of volatilization, precipitation, or coprecipitation at the higher concentrations in the final volume. The process can also be time-consuming. In spite of these problems, the process can be useful. The USEPA permits the use of evaporation for the determination of total metals in drinking water supplies.

120. Adequate precautions to prevent contamination are the use of closed chambers purged with clean air or a clean-air hood (laminar flow with HEPA filtration) and the use of sub-boiling temperatures. Infrared radiation is a preferred method of heating aqueous solutions since the energy is absorbed in and heats the top layers of the solution where evaporation occurs; the bulk of the solution remains cool, decreasing losses by volatilization.

Shallow, large surface-area vessels increase evaporation rates so that evaporation rates of 0.4 l/hr can be obtained at low sample temperatures.

121. Freeze-drying can also be used for sample concentration with excellent results. The major benefit of this technique is that the aqueous sample is sublimed at low temperatures under a vacuum. The temperature of the sample is set by the strength of the vacuum, which determines the vapor pressure of the solvent above the sample. The sample is generally taken to dryness and resuspended in a small amount of digestion fluid so that relatively large concentration factors can be obtained. The process is generally slower than evaporation at atmospheric pressure and high temperature.

Coprecipitation

122. Up to 10- to 50-fold concentration increases can be attained with coprecipitation. However, the technique has several pitfalls: (a) the process is long and tedious and can therefore be expensive; (b) contamination can occur from the precipitating agent if it is not ultrapure; and (c) the final solution can have high TDS if the carrier precipitate (or scavenging agent) is not completely redissolved during the final solubilization process, which can lead to interference problems.

123. Several carriers or scavenging precipitates have been described. Ferric hydroxide has been used for freshwater samples (Bowen 1969) as well as for seawater (Parker 1976); bismuth hydroxide has been recommended for use in trace metal analysis for lead in blood and urine. Thioacetamide has been used for trace elements in water (Mallory 1976); in this system, tin (II) sulfide was recommended as a scavenging agent for An, Bi, Cd, Cu, and Pb, whereas indium sulfide was the recommended carrier precipitate for Be, Cr, Fe, Ti, and Zn. Also used as a carrier or precipitate, thioanalide (2-mercapto-N-naphthyl-acetamide) showed recoveries in excess of 95 percent from 30-percent aqueous ethanol solution at pH 10 for Co, Cr, Hf, Hg, I, Ir, Mn, Os, Rh, Sn, Ti, and Zn.

Ion exchange chromatography

124. Cationic species can be separated from anionic interferences using traditional strong acid or strong base resins. These resins can also be used to concentrate trace metals from dilute solutions. However, ordinary ion exchange resins are of limited use in concentrating trace elements from high ionic strength solutions such as seawater, digested sludges, brines, or blood;

but specialized resins that are effective on these sample types have been developed.

125. A common resin that is commercially available, Chelex 100, is a highly purified form of Dowex A-1 and is available from BioRad Laboratory, Richmond, Calif. It is a styrene-divinylbenzene copolymer containing imminodiacetate functional groups. It is especially useful for this purpose because the selectivity of Chelex 100 is a function of the imminodiacetate functional group rather than the size or charge on the ion. The bond strength is almost 10 times greater than that of conventional strong acid resins, and it demonstrates slower exchange kinetics than other types of ion exchangers. Chelex 100 has a strong attraction for transition metal ions even from solutions of high salt concentrations. It has been used with excellent result to concentrate Cd, Cu, Ni, and Zn from seawater (Van Loon 1980) and Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn from estuarine and seawater (Kingston et al. 1978).

126. Treatment with Chelex 100 resin has been compared with APDC-MIBK extraction for the concentration of Cd, Cu, Pb, and Zn from seawater (Nygaard and Hill 1979); neither procedure was identified as superior to the other for the determination of biologically active metals. Paulson (1986) has shown that heating, ultraviolet (UV) oxidation, or reducing the column flow rate reduces the inhibition of the extraction of trace metals by organic matter in estuarine and coastal seawater. The determination of Mn, Cu, Ni, Cd, Pb, and Zn in seawater by Chelex 100 yielded high recoveries and low imprecisions and resulted in clean, quantitative, and labor-efficient procedure. Hartenstein, Ruzicka, and Christian (1985) perfected a method using a miniature ion-exchange column of Chelex 100, which increased the sensitivity for multi-element measurements in ICP-AES. This flow injection analysis (FIA-ICP) method gave simultaneous multielement detection limits that were over 20 times better than for conventional continuously aspirated systems for Ba, Be, Ca, Co, Cu, Mn, Ni, and Pb. Precision of the technique was better than 6-percent relative standard deviation (RSD) at 10-ppb level for aqueous standards and a sampling rate of 30 samples/hr.

127. The use of Chelex 100 was compared with direct preconcentration using two columns with the acrylate resin, XAD-7, for graphite furnace (GF)-AAS analysis of trace metals in fresh and seawater. The samples were first put through a XAD-7 column at pH 1 to 2 to remove organic ligands, primarily humic acids, before preconcentration of the trace metals on the

analytical column at pH 8. Precision, expressed as a relative standard deviation, averaged 10 percent over all elements (Cd, Cr, Cu, Co, Fe, Mn, Ni, and Pb), concentrations, and samples.

128. Other resins have been used to concentrate trace metals from a variety of samples. Burba et al (1979) successfully used a cellulose exchanger containing 1-(2-hydroxyphenylazo)-2-naphthol to obtain enrichments of over 100-fold for Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn from seawater and freshwater samples. They filtered 5 l of sample water through the resin column and eluted with 50 ml of 1 M hydrochloric acid. Korkisch (1978) concentrated Cd, Co, Cu, Mn, Pb, and Zn, using anion exchange on Dowex 1 from seawater samples. Preparation and use of a poly (dithiocarbamate) resin for concentration of trace metals from urine were described by Barnes and Genna (1979); concentration factors of 125 with recoveries better than 95 percent were obtained for Cd, Cu, Pb, Hg, Ni, Se, and Sn with this resin.

129. Another special resin, 8-hydroxyquinoline immobilized on silica gel, has been prepared for preconcentration of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn from seawater prior to their determination by GF-AAS (Sturgeon et al. 1981). A column technique permitted large enrichment factors to be attained (up to 500 times) while providing rapid processing of large volume samples, quantitative recovery of these elements, and a matrix-free concentrate suitable for direct analysis. The elution of the sequestered metals from the column bed was effected by using 10 ml of 1 N HCl and 0.1 N HNO₃. Marshall and Mottola (1985) studied the same procedure in a flow system for trace metal analysis by FIA-AAS. The relatively high capacities and reproducible preparation of these materials, as well as the absence of swelling complications, allow for their effective use in FIA-AAS by implementation of rather simple manifolds.

130. The chelated metal complex can also be collected onto a column of C₁₈-bonded silica gel (Sturgeon, Willie, and Berman 1985). Simple, rapid, and quantitative concentration of Se and Sb into a clean matrix are suitable for GF-AAS. Concentration factors of 200-fold are readily obtained. Poly (hydroxamic acid) chelating resins have also been used to separate Zn from Cd and Co from Cu and Ni (Shah and Devi 1987).

Electrodisposition

131. Electrodisposition has been used as a method of choice for isolating radioactive elements, but it has not found wide application in trace

metals sample preparation. Theoretically, this technique should allow the selective disposition of trace elements from a large volume of solution containing a high concentration of alkali and alkaline earth metal salts. Subsequent solubilization from the electrode should give significant enrichments in a solution of defined matrix. However, uncertainties about the matrix of the original solution and unfavorable kinetic factors for disposition lead to ill-defined decomposition potentials and have limited the usefulness of the procedure, although some successful applications have been reported (Batley and Matousek 1980).

132. Trace metals were preconcentrated from a flowing stream prior to their determination by ICP-AES (Long and Snook 1983). The metals were deposited on a glassy carbon electrode held at the reduction potential of the metals. After collection, the metal was stripped back into solution by applying an anodic-stripping potential, and the resulting metal solution was pumped directly to the ICP for determination. Ogaram and Snook (1984) have also described electrochemical cells used for preconcentration of trace elements from flowing solutions prior to their determination by ICP-AES. The cells are suitable for in-line use with the nebulizer sample introduction system of ICP. Plating efficiency was only 35 percent in the best design.

133. Habib and Sain (1985) studied both graphite electrodes and hanging Hg drop electrodes as a separation and preconcentration technique for ICP using the direct sample insertion device. With a deposition time of 5 min, the detection limits under compromise conditions were Cu, 2.4; Pb, 680; Zn, 2.0; Cd, 175; Ni, 25; and Co, 259 ng/ml. A determination of Cu at the 63-ng/ml level in artificial seawater was made with a 4-percent error.

Speciation of Trace Metals

134. In complex, natural samples such as sludges and sediments, each trace element may exist in various forms such as simple hydrated ions of different oxidation states, inorganic and organic complex ions, nonionic dissolved species, and colloids. They can also be adsorbed on, occluded in, or included in suspended inorganic, organic, or biological particulate matter. Knowledge of trace element speciation in natural and wastewaters is often necessary to assess their environmental impact and effect. This section briefly describes enrichment techniques used especially for trace element speciation.

135. Sometimes trace element speciation can be estimated by using published equilibrium data, pH, oxidation-reduction potentials, or other sample characteristics. Potentiometric measurements with ion-selective electrodes, voltammetry, and spectrophotometry are sometimes effective in directly determining the specific form(s) of trace elements present. The applicability of these techniques is often limited, however, so that selective enrichment techniques for a specific chemical form of the trace metal are the most effective methods. When using these techniques, it is important to keep in mind that equilibria between various species may be shifted upon removal of one of the species.

136. Techniques for concentrating the trace metals have already been discussed in this section. To obtain the total trace metal concentrations in natural or wastewaters, the analyst usually must separate suspended particulate matter by filtration or centrifugation, destroy the organic matter by wet or dry oxidation or ultraviolet irradiation, and/or alter the oxidation states of ions by oxidation or reduction. The separated suspended particulate matter is analyzed for the trace metals after dissolution.

137. A procedure to fractionate sludges into various chemical forms has been developed under USEPA contract by Lund, Sposito, and Page (1985), who were studying the chemical forms of trace metals in sewage sludge and sludge-amended soils. The procedure consists of extraction by successively stronger extracting solutions to partition the metals into five groups by their form in the sludges:

<u>Extractant</u>	<u>Metal Form</u>
KNO ₃	Extractable
Distilled, deionized water	Exchangeable
NaOH (0.5M)	Organically bound
Na ₂ EDTA (0.05M)	Carbonate
HNO ₃ (4N, 80C)	Sulfide-residual

They also developed a computer program to calculate trace metal equilibria in soil solutions affected by the application of sewage sludges.

Separations based upon
particle size and density

138. Filtration. Filtration is the most widely used method to separate suspended particulate matter in natural waters. The 0.45- μ m pore diameter membrane filter is commonly the method of choice to differentiate the suspended particulate matter from the dissolved or soluble fraction. Filter materials include cellulose, synthetic polymers, glasses, and metals. Problems encountered include rapid filter clogging with high solids samples, adsorption and loss of solutes on the filter matrix, contamination caused by impurities in the filter, increased airborne contamination, and the rupture of phytoplankton cells by vacuum or pressure filtration. Ultrafiltration with Diaflo Ultrafiltration Membrane UM-2 (cutoff molecular weight of about 1,000) has been used to concentrate trace elements associated with humus in lake waters (Benes, Gjessing, and Steinnes 1976).

139. Dialysis. Dialysis can be carried out on filtered samples using cellulose dialysis tubing with varying pore diameters (usually in the nanometre size range). Generally, the external, distilled water is changed periodically until a negative test for chloride or other tracer is obtained. This methodology can give information concerning the amount of metal ion complexed with large molecular weight organics. In a reverse method, dialysis tubing containing pure water can be placed in water samples or actual environmental conditions to separate the truly dissolved or available forms from the sample without otherwise disturbing it (Benes and Steinnes 1974).

140. Donnan dialysis for the enrichment of cations has been extensively studied by Cox et al. (1984). The procedure of a Donnan dialysis experiment is to preconcentrate ions from an aqueous sample across an ion-exchange membrane into a concentrated electrolyte, the receiver solution. Depending upon the charge of the fixed ionic sites on the membrane, either anions or cations can be preconcentrated. The rate of Donnan dialysis is independent of the sample matrix over a wide range of conditions so that enrichments can be performed from many kinds of samples without preliminary chemical treatment.

141. Gel filtration chromatography. Gel filtration chromatography is based upon inclusion and subsequent elution of solutes through a column containing a porous polymeric gel as a molecular sieve. With this technique, dissolved organometallic compounds such as trace metals associated with humic or other organic materials can be fractionated according to their molecular

size or molecular weight differences. For example, two distinct peaks are observed in a chromatogram of a secondary sewage effluent spiked with 700 ng of Cu--a larger, molecular weight about 10,000, fraction containing about 14 percent of the Cu, and a smaller, molecular weight about 500 to 1,000, fraction containing about 86 percent of the Cu; no free Cu was found in the sample.

142. Centrifugation. The concentration of suspended matter for digestion and direct analysis of trace metals can be accomplished with a reasonable degree of precision, accuracy, and facility by centrifugation or settling/centrifugation (Horowitz 1986). These methods produce results comparable with in-line filtration for significantly less manpower input, with fewer analytical difficulties, and at lower per sample costs.

Separations based
upon chemical reactivity

143. Volatilization. The separation of volatile species of As, Se, Sn, and Hg can often be accomplished by simple gas stripping followed by subsequent scrubbing of the gas stream. Volatile arsines such as mono-, di-, and trimethylarsines can be separated from other nonvolatile arsenic species by gas stripping with helium. Then, inorganic As(III) can be selectively converted into arsine with sodium borohydride at pH 4 to 6 and stripped from the solution. The stripped arsines are captured in a liquid nitrogen trap for subsequent analysis (Howard and Arbab-Zavar 1981). Maher (1983) describes the use of a zinc reductor column method of reducing methylated arsenic species to their respective arsines for subsequent determination in a heated carbon-tube furnace. Detection limits ($4 \times$ blank SD) were 0.006 mg/l for monomethyl and 0.001 mg/l for dimethyl arsenic.

144. Volatile dimethyl selenide and dimethyl diselenide can be separated from other nonvolatile Se species by gas stripping. They are collected in a cold trap and then separated from each other by gas chromatography. The differentiation of nonvolatile inorganic Se(IV) and Se(VI) is carried out by selectively volatilizing Se(IV) as hydride from 4 M hydrochloric acid solution with sodium borohydride. Se(VI) is quantitatively reduced to Se(IV) by simply boiling an acidified solution for obtaining the total inorganic Se value. All Se species are determined by AAS (Cutter 1978).

145. Inorganic Sn(IV) and the halides of methyltin, dimethyltin, trimethyltin, diethyltin, triethyltin, n-butyltin, di-n-butyltin, tri-n-butyltin,

and phenyltin in natural wastes are volatilized as hydrides with sodium borohydride. The hydrides are then separated from each other on the basis of their different boiling points and detected by AAS (Hodge, Seidels, and Goldberg 1979).

146. Differentiation among three species of Hg--inorganic Hg, arylmercury compounds such as phenylmercury(II) chloride, and alkylmercury compounds such as methylmercury(II) chloride--can be achieved by differential reduction with different reducing agents. Ethylenediaminetetraacetic acid (EDTA) plus hydroxylamine reduces only inorganic Hg to elemental Hg in alkaline solution; EDTA plus tin(II) chloride reduces inorganic Hg and arylmercury compounds to elemental Hg; and Cd chloride plus tin(II) chloride reduces all forms of Hg to elemental Hg. An automated system has been developed based upon this enrichment technique and cold-vapor AAS analysis (Goulden and Anthony 1980).

147. Liquid-liquid extraction. Oxidation states of several trace elements can be differentiated in natural waters by liquid-liquid extraction. Cr(VI) is selectively extracted with DDTC-MIBK or APDC-MIBK (or -chloroform), leaving Cr(III) in the aqueous phase (Bergmann and Hardt 1979). Aliquat-336 (a mixture of high molecular weight quaternary ammonium salts containing C₈ straight carbon chains)-toluene selectively extracts Cr(VI) from weakly acidic (pH 2) solutions and Cr(III) from neutral (pH 6 to 8) solutions containing at least 1 M thiocyanate (de Jong and Brinkman 1978). As(III) is selectively extracted with APDC-MIBK (or -nitrobenzene) or ammonium sec-butyl-dithiophosphate-hexane leaving As(V) in the aqueous phase (Chakraborti et al 1980). Se(IV) is selectively extracted with DDTC into carbon tetrachloride, or with 1,2-diamino-3,5-di-bromobenzene, or 4-nitro-o-phenylenediamine into toluene as piasselenol, leaving Se(IV) in the aqueous phase (Measures and Burton 1980).

148. Carrier precipitation. Different oxidation states of Cr and Se in natural waters can be separated using carrier precipitation. Cr(III) is coprecipitated with Fe(III) hydroxides precipitates leaving Cr(VI) in solution (Pik, Eckert, and Williams 1981). Cr(VI) is also coprecipitated either with barium sulfate precipitates after masking of Al, Cr(III), and Fe(III) with salicylic acid (Yamazaki 1980) or with cobalt pyrrolidinedithiocarbamate precipitates at pH 4 after removal of Cr(III) by carrier precipitation with Fe(III) hydroxide at pH 8.5 (Pik, Eckert, and Williams 1981).

149. Electrodeposition. Both Cr(VI) and Cr(III) are reduced at pH 4.7 and accumulated as metallic Cr with Hg on a pyrolytic graphite tube cathode at -1.8 V versus standard Calomel electrode (SCE), while at the same pH, Cr(VI) is selectively reduced to Cr(III) and accumulated by adsorption at -0.3 V versus SCE (Batley and Matousek 1980).

150. Sorption, ion exchange, and liquid chromatography. Ion exchange and other sorption techniques are used to differentiate oxidation states of trace elements dissolved in natural and wastewaters. For instance, Cr(VI) in natural wastes is sorbed at pH 5 on an anion-exchange resin, whereas Cr(III) is not. The sorbed Cr(VI) is then eluted with 1 M sodium chloride or a reductant solution (e.g., 0.5 M Fe(III) ammonium sulfate in 1 M hydrochloric acid) for AAS; or, Cr(VI) is selectively sorbed on a poly(dithiocarbamate) resin column (Miyazaki and Barnes 1981) or on Amberlite LA-1 or LA-2 liquid anion exchangers (Minoia et al 1983). Se(IV) can be selectively sorbed onto a macroreticular resin (Amberlite XAD-2) column as Se(IV)-DDTC complex in the presence of Se(VI) in seawater. The sorbed Se(IV) is then eluted with a dilute mixture of nitric and perchloric acids for determination (Sugimura and Suzuki 1977).

PART IV: CONTAMINATION AND LOSS OF ANALYTE

151. The problems of loss and contamination in analytical samples are intensified by the rapidly lowering absolute sensitivities of analytical methods for trace metals. Ultratrace analyses must be performed in controlled environments to protect the sample from artifacts contributed by laboratory air and unclean containers. Care must be taken in the selection and cleaning of sampling devices and sample containers, in collecting the samples and ensuring their integrity with specific preserving agents, and on placing of strict limitations on holding times and conditions. Similar precautions also apply to the routine laboratory operations in sample preparation. Handling as well as containment of the sample during preconcentration and separation procedures is a most critical step in a determination at trace and ultratrace levels, but samples are subject to contamination or loss at essentially any point in the collection-analysis process (USEPA 1979c). A perfect analysis of an improper sample is a futile exercise.

Purity of Analytical Reagents

Laboratory water

152. Ideally, water should be invisible to analyses or at least free of problem impurities that could affect the accuracy or interpretation of the results. This depends of course on the laboratory application. Pure water is a highly aggressive solvent that degrades during contact with air, distribution piping, storage reservoirs, or virtually anything else it touches. It is therefore not something that can conveniently be stored or carried in a flask from some other location.

153. Several professional organizations have published standards for laboratory water, usually called Type I Reagent Grade Water. A summary of these specifications is shown in Table 16. Type I water should be specified when a minimum level of ionized contaminants is essential, as it is in trace metal analysis. Various types of treatment are available alone or in sequence to produce high quality water. Table 16 illustrates three different, common water purification specifications. A system that produces water on demand at a convenient location is usually preferred over a central water system.

Table 16
Summary of Specifications for Type I Reagent Grade Water

Attribute	ACS*	CAP and NCCLS*	ASTM*
Specific conductance (micromhos, max)	-	<0.1	<0.06
Specific resistance (megohm, min)	>0.5	>10	>16.67
Total matter (mg/l)	-	-	<0.1
Silicate (mg/l)	<0.01	<0.05	Not Detectable
Potassium permanganate reduction** (min)	>60	-	>60
Culture/colony count	-	<10	†
Heavy metals (as Pb ng/ml)	<0.01	-	-

* ACS = American Chemical Society (for Reagent Grade Water).
 CAP = College of American Pathologists.
 NCCLS = National Committee for Clinical Laboratory Standards.
 ASTM = American Society for Testing and Materials; ASTM specifies
 distillation pretreatment for Type I water.

** ACS: to 500 ml, add 1 ml of sulfuric acid and 0.03 ml of 0.1 N permanganate; allow to stand for 60 min at room temperature; the color should not be entirely discharged. ASTM: add 0.40 ml of 0.01 N permanganate.

† ASTM specifications for bacteria: Type A: 0; Type B: <10; Type C: <100.

Reagent purity

154. No single quantitative definition of purity or ultrapurity has been universally adopted by the scientific community (Zief and Mitchell 1976), even though these levels can set the limit of systematic errors. Many preconcentration processes also concentrate reagent impurities. Terms such as super pure, spectrographically pure, or ultrapure have no universal meaning. All reagents must be accompanied by an actual lot analysis including method of analysis and detection limits as well as certified data for the trace elements of specific interest (see Table 17).

155. The end use of the reagent determines the level of purity required. The electronics industry was one of the first to discover the importance of impurities in the early semiconductor work where ultrapure metals with impurity levels in the low nanogram per gram (10^{-9}) range are

Table 17
Analysis of Water for Cations,* ng/g

Element	Water Samples**			
	A	B	C	D
Ca	>10,000	50	1.0	0.08
Cd	-	-	<0.1	0.005
Cr	40	-	<0.1	0.02
Cu	30	50	0.2	0.01
Fe	200	0.1	0.2	0.05
Mg	8,000	8.0	0.3	0.09
Na	10,000	1.0	1.0	0.06
Ni	<10	1.0	<1.0	0.02
Pb	<10	50	0.1	0.003
Zn	100	10	<1.0	0.04

* Taken from Millipore Corp. Bulletin MB-403, "Super-Q System," (1973).

** A = tap water, Phillipsburg, N. J., B = tap water purified by two-stage commercial metal still; C = tap water purified by train of carbon, mixed-bed resins and 0.2- μ cellulose acetate filter; D = deionized water purified by subboiling distillation. Sample D analyzed by isotope dilution, others by AES after concentration of 1,000-ml sample.

commonly required. Organics in the ultrapure classification typically have a minimum purity of 99.85 percent, i.e., 500,000 ng of impurities per gram.

156. Commercial high purity reagents are usually available for most analytical techniques. If not available or too expensive for routine use, high purity reagents can be prepared in the laboratory. In many cases, classical techniques such as crystallization, fractional distillation, or liquid-liquid extraction produce sufficient purity. Often one method may serve for prepurification and a second method for ultrapurification. Common sources of impurities in laboratory procedures are from airborne particles, heating elements in drying ovens, or washing of precipitates. Analysis of reagent samples before and after purification must be carried out to prove the effectiveness of the purification procedures. Often these monitoring efforts set the limit on the degree of purity that can be proven since purity below instrument detection limits cannot be proven and analysis may be a major expense.

Control of Contamination

Airborne contamination

157. Aerosols composed of solid and liquid particulate matter are common constituents in the ambient air. Other suspended solids are derived from natural sources such as mineral dusts, pollen, or spores and from man-made sources. A 7-year analysis of airborne particulates showed a 24-hr mean of 98 and maximum of 1,706 $\mu\text{g}/\text{m}^3$ (Morrison 1973). The mean and maximum values in the same units were Fe, 1.9 and 74; Pb, 0.5 and 17; Zn, 0.09 and 58; sulfate, 9.3 and 95.3; and nitrate, 1.6 and 24.8. A single dust particle can weigh up to 1 μg . Trace elements in laboratory dust have been reported (in mg/kg): As, 55; Cd, 3; Cr, 39; Cu, 213; Fe, 3,230; Mn, 116; Ni, 70; Pb, 2,150; and Zn, 1,640 (Sansoni and Iyengar 1980). Dust contamination has been suggested as a major source of analytical inaccuracies in trace elemental analyses (Katz 1984). Adeloju, Bond, and Briggs (1985) devised a method to assess the effects of air quality on trace and ultratrace determination of Cd, Se, Cu, Zn, Ni, and Co. Significant contamination of all metals except Cd were experienced at the sub-parts-per-billion level.

158. Existing laboratories can be upgraded with minimum alterations and with no loss in existing bench space. A two-step procedure has been recommended (Zief and Mitchell 1976). In the first step, the general laboratory space is upgraded. For a minimum approach, all incoming air from air-conditioning, heating, and ventilating sources are filtered with a 85- to 95-percent efficient filter. These filters are 85-percent efficient for 0.5- to 5- μm particles and 95-percent efficient for particles greater than 5 μm . The filters should be placed at existing air outlets (which have been enlarged to minimize the reduction in linear air velocity caused by filter friction). Air ducts should be cleaned of accumulated dust, and filters should be checked at regular intervals. Other precautions include removal of all metallic insulations and the painting of walls, ceilings, pipes, and other metallic parts with a nonabrasive, metal-free paint (Adeloju, Bond, and Briggs 1985).

159. The second step centers on further cleaning air supplied to critical work areas by the use of high efficiency particulate air (HEPA) filters. Standard HEPA filters have a minimum efficiency rating of 99.97 percent for 0.3- μm particles. Dust control hoods and laminar-flow work stations are recommended for localized activities in the analytical laboratory and provide

dramatic improvement in blank values and variation. See Adeloju, Bond, and Briggs (1985) for a demonstration of the importance of a clean room environment in ultratrace metal analysis. In designing a new laboratory or major modifications to existing laboratories, particular attention should be given to particulate removal from the circulating air. Excellent clean room conditions can be provided by well-planned design, such as using HEPA filters in a large area of the laboratory ceiling or in one wall. Several designs have been discussed in Zief and Mitchell (1976).

Storage of chemicals and samples

160. Changes in trace metal levels during storage of reagent chemicals, dilute reagent blanks, and complex samples are major sources of error. Major problems arise from evaporation of the solvent or volatile component, leaching from or adsorption to container materials, and chemical reactions within the container (as with oxygen). The problems contributed by walls of containers rival those induced by laboratory air. The concentrations of extractable Cu, Zn, Fe, and Mn in oxidized estuarine sediments have been found to be strongly influenced by the manner and time of storage between collection and extraction (Thompson et al. 1980). No storage method tested completely preserves the initial chemical and physical characteristics of the sediment. Adequate methods of storage are freezing or (for some extraction) drying if the sediments are to be extracted only with acids. However, if a variety of extractants are to be used as in studies of metal speciation, extraction should be conducted as soon as possible after collection.

161. The relative suitability of container materials, in ascending order, for trace analysis applications includes: polyfluorocarbons > polyethylene > vitreous silica > platinum > borosilicate glass. This rating reflects primarily the order of decreasing container contamination; i.e., polyfluorocarbons show a greater tendency for contamination than polyethylene, etc. Table 18 summarizes the most important properties of these container materials for the analytical laboratory, and Table 19, the preferred materials for different analytical apparatus. A complete discussion of these materials and their application is found in Zief and Mitchell (1976).

162. The reduction of Cr(VI) during storage of water samples preserved by standard techniques (USEPA 1979a, APHA 1985) indicated that a significant reduction of Cr(VI) was likely to occur at the acidic pH's recommended (<2). The best method of preservation to retain Cr(VI) is immediate filtration

Table 18
Properties of Container Materials for Trace Metal Analysis*

Material	Temp Limit (°C)	Chemical Resistance to			
		10% HF	10% HCl and 10% HNO ₃	10% NaOH	Halogenated Hydrocarbons
Polyfluoro- carbons	250	Exc**	Exc	Exc	Exc
Polyethylene linear conven- tional	110	Exc	Exc	Good	Poor
	80	Exc	Exc	Good	Poor
Vitreous silica	1,100	Poor	Exc	Poor	Exc
Platinum	1,500	Exc	Exc	Exc	Exc
Borosili- cate glass	800	Poor	Exc	Poor	Exc

* Adapted from Zief and Mitchell (1976).

** Exc = excellent.

Table 19
Preferred Materials and Their Use in Ultra Trace Analysis*

FEP	Teflon		Polyethylene (Conventional)	Vitreous Silica
		TFE		
Reagent bottles		High pressure bombs	Wash bottles	Evaporating dishes
Beakers		Bottles for pressure filtration	Storage containers for water	Pipets and scopes
Separatory funnels		Pressure filter apparatus	Bench top cover filters	Envelope for magnetic stirrers
Resin columns		Beakers	"Clean" bags	Dishes for micro- wave drying; boats, muffles for furnaces

* Adapted from Zief and Mitchell (1976).

(0.45- μ membrane), refrigeration, and analysis as quickly as possible
 (Stollenwert and Grove 1985). The rate of reduction of Cr(VI) to Cr(III)

increases with increasing NO_2 , dissolved organic carbon, H-ion concentration, and temperature. Water samples should not be acidified.

Cleaning of Laboratory Glassware

163. Improperly cleaned glassware is a frequent source of contamination. The USEPA (1982) includes the following procedure for cleaning glassware, plastic containers, and sample tubes:

- a. Thoroughly scrub with detergent and water.
- b. Rinse with a 1:1 solution of HCl and water.
- c. Rinse with water.
- d. Rerinse with a 1:1 solution of HCl and water.
- e. Rinse with water.
- f. Rinse with distilled, deionized water.
- g. Dry plastics at 50° C and glassware at 105° C.

164. Conflicting reports on the cleaning and storage methods for samples in polyethylene were studied for Zn, Cd, Pb, and Cu by Laxen and Harrison (1981). Their comparison of cleaning methods gives a better basis for choice of cleaning methods for polyethylene sample containers. They recommend that a 48-hr soak with 10-percent nitric acid be used for preliminary cleaning of new bottles and for routine cleaning.

Adsorption and Volatilization of Analytes

165. The adsorption of analyte on the surfaces of containers and the volatilization of analyte from the containers have been identified as major contributors to analyte losses (Behne 1981). Adsorption losses to the walls of the sample containers are retarded by the addition of appropriate preservatives, but volatilization losses during heating and handling of the sample are of serious concern, especially for the volatile trace elements like Hg.

166. Ashing aids may be used to reduce volatilization and/or adsorption. Magnesium nitrate is used extensively for this purpose and can increase the recovery of some trace elements after dry ashing. However, contaminants in the magnesium nitrate can be confused with additional recovery. It is necessary to establish blank values whenever ashing aids or fusion mixtures are used. The loss of analyte, unlike the introduction of contamination,

cannot be determined from blank values. Recovery studies in which known amounts of analyte are carried through the dry ashing procedure are used to evaluate volatilization and adsorption losses. In some cases, samples are split and spiked, and recoveries are calculated from the differences between the results obtained from the spiked and the unspiked, split samples. However, it is important to realize that the spike additions may have different volatilization rates if they are not in the same chemical form as the original sample.

PART V: MATRIX EFFECTS AND BACKGROUND CORRECTION IN AAS AND AES

167. AAS and AES exhibit high selectivity and sensitivity. However, in complex samples, several properties of the sample matrix, analyte, sample injection technique, and resonance radiation interfere with accurate comparison of sample absorption or emission with that of the standard. These interferences are usually broken into spectral, physical, and chemical types. The later two are often combined as physiochemical interference as they are often difficult to distinguish between. Their effects on standard comparisons can be minimized by matrix matching and/or background correction.

Spectral Interferences

168. Spectral interference is concerned with detection of radiant emission or absorption that is not related to the presence of the analyte. This is especially important to AES analysis since the analysis line must be differentiated from adjacent lines, bands, or ionic spectra of other materials present in the sample and from the background continuum from the flame or plasma.

Atomic emission

169. Atomic line interference is particularly severe in atomic emission (AE) analysis and may preclude trace analysis of metals in complex matrices by this method. The lines of major intensity are shown in Table 20, but innumerable weak lines may be important in specific analyses. A complete listing of all major and minor bands for all constituents is presented by Parsons, Forster, and Anderson (1980). Preanalysis separation techniques may be necessary to remove the interfering element. At elevated temperatures, ion lines may also interfere (see ionization energies listed in Table 21), but the addition of ionization buffers can be used to suppress these effects.

170. Broad spectral band interferences can originate from sample matrix components or from flame chemicals. Some common molecular band ranges are shown in Table 22. Oxides produced within the flame (for those species with oxide dissociation constants greater than about 5 in Table 21) and produced from organic solvents will also produce band interferences. These also demand pretreatment of samples to remove the responsible species.

Table 20
Major Spectral Interferences in AE Spectrometry*

Element	Line, nm**	Interferent	Line, nm†	Reference ††
Ag	328.07	Cu	327.40	1
	(338.29)	Ni	338.1 ^a	2
As	(234.98)	Be	234.86	2
Au	267.60	OH	260.9 ^b	2
Bi	306.77	OH	b	2
	(289.80)	OH	b	2
Cd	(326.11)	Sn	326.23	2
		OH	326.1 ^b	2
	228.80	As	228.81	2
Co	345.35	Ni	345.29	2
			345.85	2
	(350.2) ^a	Ni	c	1
		Mn	353.20	1
	(387.31)	CH	387.2 ^b	2
	(387.40)	MgOH	387.7 ^b	2
Cr		Fe	387.25	2
	357.87	Co	c	1
	425.43	Co	425.23	2
Cu		CH	424.9 ^b	2
	324.75	Ni	323.30	1
			324.31	1
	327.40	Ag	328.07	2
Fe		OH	327.42	2
	371.99	MgOH	371.9 ^b	2
Ga	(403.30)	K	404.41	1
		Mn	403.31	1
	417.21	BO ₂	418.0 ^b	2
In	410.18	SnO	b	1
	451.13	Mo	d	2
		BO ₂	453.0 ^b	2

(Continued)

* Adapted from Burrell (1975).

** Minor analysis lines are in parentheses.

† a = Doublet; b = Band; c = Series; d = Continuum; e = Triplet.

†† References: 1 = Cresser and West (1970); 2 = Buell (1969); 3 = Dean and Simms (1963).

Table 20 (Concluded)

Element	Line, nm**	Interferent	Line, nm†	Reference††
Mn	403.08	Ga	403.30	2
		CH	403.4 ^b	2
	(403.31)	K	404.41	1
		Ga	403.30	1
Mo	379.83	MgOH	b	2
		Ru	379.89	2
Ni	(341.48)	Co	c	1
	352.45	Co	c	1
		Mn	c	1
	(301.94)	Fe	c	1
		Cr	c	1
Pb	405.78	Mn	405.7 ^a	2
		Cu, CuH	406.2 ^b	2
		CH	406.0 ^b	2
Pd	340.46	Co	340.51	2
Rh	369.24	Sn	309.14	2
Ru	(372.69)	MgOH	372.9 ^b	2
	372.80	MgOH	372.9 ^b	2
Sb	259.81	Po	259.6 ^b	2
Sn	(317.50)	OH	317.5 ^b	2
Te	238.6 ^a	Fe	c	3
Tl	377.57	Ni	377.56	2
		MgOH	376.7	2
		BaO	b	1
		Fe	c	1
		Ni	377.56	1
V	318.54 ^e	OH	318.5 ^b	2
Zn	(481.05)	Sr	481.19	2

171. Spectral interferences for AE can be eliminated or suppressed to a large extent by using one or more of the following techniques:

- a. Preanalysis separation of interference or analyte.
- b. Use of optimized buffers and solvents or flames.
- c. Background scanning.
- d. Optimization of monochromator resolution.
- e. Pulsing sample into the flame with a tuned detection system.

Table 21

Ionization and Dissociation Energies of Metal Oxides and Degrees of
Ionization Computed at Two Standard Flame Temperatures*

Element	Energy, eV		Degree of Ionization, %	
	Ionization	Dissociation	Air-Acetylene (2280C)	N ₂ O-Acetylene (2930C)
Ag	7.57	1.4	---**	1.6
As	9.81	4.9	--	---**
Cd	8.99	3.8	--	0.2
Cr	6.76	4.2	0.3	8.5
Cu	7.72	4.9	--	1.2
Fe	7.78	4.0	--	1.6
Hg	10.43	-	--	--
Mn	7.43	4.0	0.1	3.1
Ni	7.61	-	--	1.1
Pb	7.42	4.1	0.1	4.0
Se	9.75	3.5	--	--
Zn	9.39	4.0	--	0.1

* Adapted from Burrell (1975).

** Less than 0.1 percent.

Table 22

Some Common Band Interferents*

Complex	Wavelength Range nm	Examples of test metals affected (line)
MgOH	360 - 400	Fe 372
CaOH	543 - 622	(Ba 553.6)
(CuH)	400 - 470	Mn 403.1 Pb 405.8
(BO ₂)	400 - 670	MnO 539.0
(SrOH)	600 - 700	(Li 670.8)

* Adapted from Buell (1969).

f. Using second flame with high concentration of interferent to absorb the interfering emissions from the original flame.

172. ICP sources can have significant spectral interferences because of the greater number of lines excited by the very high temperatures in the

plasma arc. Spectral interferences from the ICP have been classified into several categories (Mermet and Trassy 1981): (a) total overlap of at least two lines, (b) lines not being fully separated without a high resolving power, (c) partial overlap resulting from line broadening, and (d) stray light. Line broadening is caused by collisions within the plasma, rapid motion (Doppler broadening), and collisional (pressure) broadening. In many cases, spectral interferences can be predicted from ICP emission tables (Boumans 1980). Some instruments display data graphically so that a scan near the detection line will show possible interferences.

Atomic absorption

173. Spectral interferences occur when radiation other than the resonance line of the analyte contributes (or detracts from) the absorbance. These occurrences are not as likely to cause undue difficulties in AAS analysis, although they are frequently cited in the literature. The few documented spectral interferences are listed in Table 23.

174. The effect of analyte ionization on AAS using a graphite furnace has been shown to be small compared with that in flame AA (Sturgeon and Berman 1981). This was attributed to the different time and temperature dependences of the atom and ion populations as well as the high background concentration of free electrons generated in the furnace.

Table 23
Spectral Interferences in Atomic Absorption*

<u>Element</u>	<u>Line, nm**</u>	<u>Interferent</u>	<u>Line, nm</u>	<u>Reference†</u>
Cu	324.754	Eu	324.753	1
Fe	(271.903)	Pt	271.904	1
Ga	(403.298)	Mn	403.307	2
Hg	253.652	Co	253.649	3
Zn	213.856	Fe	213.859	4
		Na	-	5

* Taken from Burrell (1975).

** Minor bands are in parentheses.

† References: 1 = Fassal, Rasmuson, and Cowley (1968); 2 = Manning and Fernandez (1968); 3 = Allan (1969); 4 = Kelley and Moore (1973); 5 = Kahn and Schallis (1968).

175. More serious are the various nonspecific (molecular) background absorption effects on the source lines. Compensating continuum sources are commonly used to detect and correct for these background effects. Interferences from flame emission are in AA analysis by modulating the incident resonance source at a frequency tuned to the detector system that subtracts out the constant (or untuned) signal from the flame or other background emission.

Chemical Interference

176. Physical (nonspecific) and chemical (specific) interferences are difficult to separate. Chemical interferences occur when the analyte combines with components of the matrix to form compounds that undergo atomization differently from the standards. Both AAS and AES show the effects of this type of interference.

177. A classical example of chemical interference with atomization is that of phosphate from the matrix affecting the degree of atomization of the sample when calcium nitrate or calcium chloride standards are used; calcium pyrophosphate formed in the flame is more stable than the other salts (Weberling and Cosgrove 1965). When the standard and sample (with phosphate) are compared, fewer free calcium ions are in the aspirated sample so that its signal is correspondingly lower. This type of chemical interference can be minimized by using hotter flames or plasma or by adding reagents that form easily atomized analyte to both the sample and the standard. In the case cited above, lanthanum chloride added to the sample will react with the phosphate to form lanthanum phosphate that frees the calcium to ionize at the lower flame temperatures. Alternatively, addition of EDTA also prevents the formation of calcium phosphate by binding the calcium. EDTA has found more recent use in reducing the interference from Ni, Pb, Cu, and Ag in cold vapor AAS from flyashes (Bernth and Vendelbo 1984).

178. Weisel et al. (1979) have devised a modified standard addition method for overcoming the high salt concentration while determining Cd, Cu, Pb, and Fe in seawater by AAS. Interference with trace metal analysis brought about by high salt concentrations is not totally correctable by optimizing furnace conditions and/or using background corrections. Their calculations are based upon standard curves made in the presence of high sodium concentrations that were found to correct well with the true trace metal

concentration. Slavin (1980) reviewed the literature on trace metal analysis in seawater. AA using the graphite furnace was found to be the most widely accepted method, usually after extraction into organic solvent and back extraction into acid.

179. Also sometimes classified as chemical interference is the loss of a volatile analyte compound during drying or ashing steps in electrothermal atomization. For instance, when lead nitrate standards are used, samples containing chloride will show low results because of the loss of lead chloride formed in the matrix during heating. Interferences of this type can be determined by splitting and spiking or quantitatively estimated by using the method of standard addition. The sample matrix can also be modified by chemical means to prevent the formation of the volatile compound.

180. Matrix interferences also occur in Heated Graphite Atomizer (HGA) when a very volatile analyte is determined in the presence of a relatively nonvolatile matrix. It is impossible to remove an interfering matrix during the char step without also volatilizing the analytes resulting in matrix residues being volatilized during atomization and background absorption or matrix interferences. Modification of the matrix by adding reagents directly to the sample in the furnace permits either a decrease in the volatility of the analyte or increases the volatility of the matrix. Adding Ni as a matrix modifier in Se analyses reduces the volatility of the Se so that most of the matrix interference can be removed in the char step. This is due to the formation of Ni selenide, which in the furnace is a much less volatile form of Se. The addition of Ni, Ag, or Cu was found to stabilize Se(IV) at the 0.5-mg/l concentration level to ashing temperature as high as about 1,200° C (Kirkbright, Hsiao-Chuan, and Snook 1980). Addition of 0.05-percent $H_2Cr_2O_7$ (w/v) extended maximum permissible ashing temperature for Hg to 250° C. Ni (at 0.05 percent) has been used as a matrix modifier in the direct flameless AA of As. Ca was also useful to minimize matrix effects in both fresh and estuarine waters (Stein, Canelli, and Richards 1980).

181. An external sampling tube atomizer (ESTA) was used to lower volatilization interferences in electrothermal AAS by Marinescu (1984). The ESTA is used to vaporize the sample, which is then atomized in the main vessel. Marinescu (1984) successfully recovered 8 ng of Pb in the presence of 50,000-fold excesses of NaBr, KCl, $BaCl_2$, Na_2SO_4 , $MgSO_4$, and other interfering solutions.

182. Potassium iodide was found to be the most satisfactory method of reducing the interference from metals in the hydride generation AAS of As, except for Ni, Co, and Pt (Yamamoto, Yamamoto, and Yamashige 1984). Other masking agents that have been shown to be effective and were compared were thiosemicarbazide, thiourea, EDTA, tartaric acid, and citric acid. Sodium tetrahydroborate was found to selectively reduce As at low concentration.

183. A more subtle form of chemical interference occurs when the matrix inhibits or promotes the formation of ionized species that add or detract from the amount of free atoms of the analyte present. This has been termed ionization interference by Arellano, Routh, and Dalager (1985) and is very prevalent in plasmas because of their very high temperatures. Ionization can be suppressed by the addition of a more readily ionized metal to the solution, which shifts the equilibrium in the direction of the neutral atoms of the less readily ionized metal and hence increases emission or absorption. At low concentrations, a significant number of, for example, potassium atoms undergo ionization in the flame or furnace. The presence of high levels of sodium in the matrix will suppress this ionization, giving high values when compared with potassium chloride standards. In this case, large amounts of sodium chloride could be added to both the sample and the standard. Ionization buffers should be used in analysis of low levels of alkali and alkaline earth metals, especially when high temperatures are used to overcome phosphate interferences. Lithium nitrate (0.25 M) has been used as an ionic buffer for multielement DC plasma-AES (Frank and Peterson 1983). They also studied spectral interferences and stray light effects.

184. Matrix effects of high salt concentrations in brine solutions of up to 37.5-percent NaCl were overcome by precipitation for ICP-AES (Buchanan and Hannaker 1984). The Mg present in the brine solutions was used as a carrier of trace elements by adjusting the pH between 8.0 and 9.0 with sodium hydroxide. The redissolved precipitate was then accurately analyzed for 14-cation and 3-anion species. Elemental concentrations lower than 4 ng/ml were observed for many of the elements tested when using 200 ml of original brine solution.

Physical Interferences

185. Physical interferences come about by differences between the physical properties affecting the nebulization/atomization of the standards and those of the samples. Both flame and furnace techniques suffer from physical interferences. Matrix matching, matrix modification, and background correction are often employed to minimize these effects. The standard additions method can also be used to minimize the effects of these interferences.

186. Another type of physical interference is due to the retention by occlusion of the analyte in an excess of less volatile matrix compounds, or covolatilization with a more volatile matrix substance. The former causes a negative interference, whereas the latter causes an enhancement (or positive interference). A systematic investigation of the interference of 1 to 1,000 ppm of chlorides, nitrates, phosphates, and sulfates of H, Na, K, Ca, Mg, Zn, and La (except for CaSO_4) on Cu and Mn analyses was performed by Smeyers-Verbeke et al. (1976) using graphite furnace AAS. They showed that the interferences, while complex, were at least partially due to occlusion of the analyte in the less volatile matrix. Examples of interferences are shown in Table 24.

187. Differences between the sample and the standard in terms of viscosity and surface tension will affect their aspiration, nebulization, and ultimately, atomization. Matrix matching or matrix modification by solvent extraction, sample dilution, or addition of specific chemical reagents to both samples and standards will often remedy these effects.

188. The formation of a particulate cloud or combustion product vapor from the sample matrix during atomization gives rise to scatter or absorption of the resonance or emission radiation, resulting in false absorption or lower emission from the sample. False absorption can often be treated by background correction rather than by matrix matching or modification.

189. Background corrections are made by measuring the attenuation of both the resonance line and a nearby reference line (or Zeeman broadening) as they pass the chamber. The correction is made by attributing the attenuation of the resonance line to both the analyte and interference and the reference line only to interference.

Table 24
Examples of Interferences Observed in the Flameless AAS
Determination of Mn and Cu (expressed as %)*

Salt	Ion	Effect on 50-ppb Mn of		Effect on 100-ppb Cu on	
		100-ppm ion	1,000-ppm ion	100-ppm ion	1,000-ppm ion
CaCl ₂	Ca	-80	-95	-25	-40
Ca(NO ₃) ₃	Ca	+20	+30	0	0
CaHPO ₄	Ca	+10	-25	0	-20
MgCl ₂	Mg	+50	-80	-20	-60
Mg(NO ₃) ₃	Mg	+40	+40	+10	-10
MgSO ₄	Mg	+35	+40	+30	+40
MgHPO ₄	Mg	+20	-15	+10	+10
NaCl	Na	0	0	-20	-30
NaNO ₃	Na	0	0	0	0
NaSO ₄	Na	+25	+20	-15	0
NaPO ₄	Na	0	-20	0	0

* Taken from Smeyers-Verbeke et al. (1976).

Background Absorption in Graphite Furnace AAS

190. The AAS process is said to be virtually free of spectral interferences caused by the high specificity of the primary source lamps. Another type of interference is especially common to the graphite furnace technique -- background absorption. This is caused by matrix components remaining in the furnace during atomization such as molecular species, small salt particles, or smoke. These may absorb or scatter the light emitted from the primary source lamp. Efficient thermal destruction in the graphite furnace of the matrix is limited by the fact that the temperature at which the analyte is volatilized must not be reached prior to atomization. This is especially true for volatile elements in a matrix of materials with similar volatility where even an optimal graphite furnace design, e.g., a L'vov platform, is not sufficient to separate the matrix from the analyte prior to atomization.

191. Background absorption is nonspecific in that it covers broad wavelength ranges. Correction for this background absorption is necessary to avoid erroneously high analytical results. Two techniques are typically used to overcome this problem: continuum source background correction with a deuterium arc or a tungsten halide lamp or Zeeman-effect background corrections.

The Smith-Hieftje system is a recent introduction to background corrections. These three systems have recently been compared by Liddell et al. (1986).

192. Continuum source background correction. For this method, a continuum source (usually a deuterium arc) is aligned in the optical path of an AAS so that light from the continuum source and light from the primary source are transmitted alternately through the graphite furnace. The narrow-band emission from the primary source is affected by both scatter and background absorption in addition to the absorption of the analyte, while the broad-band emission of the continuum source is affected by the background absorption only. Comparing the two signals electronically permits subtracting the background component of the primary source signal and corrects for, or substantially reduces, the erroneous background signal.

193. The determination of Pb in organic matrices illustrates the application of the continuum source background correction. Samples are diluted with a surfactant solution and measured against Pb standards prepared in dilute nitric acid. Background correction is necessary to eliminate the small nonspecific absorption signal from the matrix that remains after charring the sample at 525° C for 50 sec, higher charring temperatures causing losses of the Pb analyte (Perkin-Elmer Corp. 1981). Continuum source background correction provides excellent results for many sample analyses when used with the graphite furnace. However, accuracy of the correction decreases when the dynamic background signal level exceeds approximately 0.7 absorbance units or the interference is due to structured background absorption.

194. The Zeeman effect. Under the influence of a strong magnetic field (e.g., 10 kG), an atomic spectral line that is emitted or absorbed by an atom splits into three or more polarized components. By modulating the magnetic field in synchronization with a rotating polarizing filter, the spectral line components that represent only the background can be subtracted from the total signal, resulting in an accurate determination. It has been claimed that Zeeman background correction can accurately correct for levels of background absorption up to 2.0 absorbance units (Perkin-Elmer 1981). Other techniques use a constant magnetic field and alternately polarize the primary source beam parallel and perpendicular to the magnetic field so that the parallel beam includes both background and analyte absorption and the perpendicular beam only background absorption (Hatachi, Ltd. 1983). Further, the background

correction uses only wavelengths at the exact analyte wavelength that removes any possible errors from structured backgrounds.

195. The Smith-Hieftje system. A new method of background correction in AA spectrophotometry has been introduced by Smith and Hieftje (S-H) (1983). The technique is based upon the line broadening that occurs when a hollow-cathode lamp is run at high currents. Under such conditions, the absorbance measured for the narrow (atomic) line is low, whereas the apparent absorbance caused by a broad band background contributor remains as high as when the lamp is operated at conventional current levels. Background correction can therefore be effected by taking the difference in absorbances measured with the lamp operated at high and low currents. The detection limits using the S-H system are slightly poorer than those obtained under conditions where no background correction is employed.

196. The S-H system is applicable to flame or furnace atomizers and is claimed to correct for backgrounds caused by molecular absorption, particulate scattering, and atomic-line overlap, even up to an absorbance value of 3. The S-H system has all of the advantages of the Zeeman approach over the deuterium arc method in that it applies its correction very near the atomic line of interest (accurate corrections are made for structured backgrounds), it employs single-beam optics, and it requires no auxiliary light source (Sotera and Kahn 1982). However, the S-H method also has significant advantages over the Zeeman method: no ancillary magnets or other peripherals are required, no loss of light is caused by polarizers, the working curves are single valued, and all resonant wavelengths (visible as well as UV) are usable with existing sources. The S-H system is, by its nature, less expensive than a deuterium arc system and much less expensive than a Zeeman system; however, it is not practical to retrofit the S-H system into existing AA units because major changes in electronics are required.

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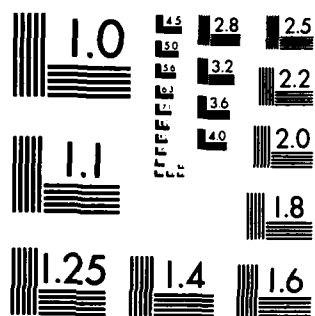
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APPENDIX A: GENERAL REFERENCES

Key to Methods Listing after Reference

AAS-Zeeman	AAS-Z
Atomic Absorption Spectrometry	AAS
Atomic Emission Spectrometry	AES
Atomic Fluorescence Spectrometry	AFS
Carbon Bed Atomic Absorption Spectroscopy	CB-AAS
Carbon Furnace Atomic Absorption Spectrometry	CF-AAS
Chelex-100	C-100
Cold Vapor AAS	CV-AAS
Column Chromatography	CC
Continuum-Source Atomic-Absorption Spectrometry	CS-AAS
Direct Aqueous Injection	DAI
Direct Current Plasma-ES	DCP-ES
Direct Current Plasma	DCP
Electrothermal Atomization	EA
Extraction Chromatography	EC
Flame Atomic Absorption Spectrometry	AAS-F
Flow Injection Analysis	FIA
Gas Chromatography	GC
Gas Diffusion Flow Injection Analysis	GD-FIA
Graphite Furnace Atomic Absorption Spectrometry	GF-AAS
Graphite Rod Vaporization	GRV
High Performance Liquid Chromatography	HPLC
Hydride Generation Atomic-Absorption Spectrometry	HG-AAS
Indirect Photometric Chromatography	IPC
Inductively Coupled Plasma	ICP
Instrumental Photon Activation	IPA
Internal Reference Method	IRM
Ion Chromatography	IC
Ionic Fluorescence Spectrometry	IFS
Laser Enhanced Ionization Spectrometry	LEIS
Ligand Substitution Reaction	LSR
Liquid Extraction & Spectrophotometry	LE-S
Low-Contamination Digestion Bomb	LCDB

Mass Spectrometry	MS
Microsampling Cup-AAS	MC-AAS
Microwave Induced Plasma	MIP
Multielement AAS	M-AAS
Neutron Activation Analysis	NAA
Nonsuppressed Ion Chromatography	NIIC
Optical Emission Spectrometry	OES
Plasma Chromatography	PC
Plasma Emission Spectrometry	PES
Plasma Source Mass Spectrometry	PSMS
Platform Furnace-AAS	PF-AAS
Polarization Spectroscopy	PS
Reverse-Phase Paper Chromatography	RpPC
Spark Source Mass Spectrometry	SSMS
Spectrophotometric Multicomponent Analysis	SMA
Spectrophotometric Detection	SsD
Thin-Layer Chromatography	TLC
Wavelength-Modulated Atomic Absorption & Emission	WMCS-AAS
X-Ray Energy Spectrometry	XES

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Metals: Cu, Pb. Method: AAS.
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Metals: Ag, Au, Al, Bi, Cd, Cr, Cu, Hg, Mn, Pb, V, Zn. Method: GF-AAS-EA.

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Method: ICP-ES.

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Metals: Fe, Cu, Zn, Mn, Al, Cr. Method: ICP-ES.

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Metals: Pb, Cd, Hg, Co, Ni, Cu. Method: HPLC.

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Method: AAS, ICP-ES.

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Method: ICP-AAS.
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Method: ICP-ES.
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Metals: Al, Ba, Cd, Ca, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Au, Ho, Fe, Pb, Li, Lu, Mg, Mo, Ni, Pd, Pt, K, Rb, Sm, Ag, Na, Sr, Tb, Tm, Sn, W, U, Yb, Zn.
Method: IC.

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Metals: Ni, V, S. Method: ICP-ES, AAS-F.

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Metals: Cd, Zn, Se. Method: AES.

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Metals: Cd, Pb. Method: GF-AAS.

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Metals: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ge, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Ru, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, Zn. Method: AAS-Z.

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Metals: Hg. Method: GF-AAS.

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Metals: Al, Fe, Mn, Be, Cd, Cr, Co, Cu, Pb, Ni, Ag, Tl, Zn, Bi, Au, In, Mo, Re, Th, Sn, W, U, V, Zr, Hg, Sb, As, Se, Te, B, P, Si. Method: EA, CV- AAS, AAS.

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Metals: Ca, Mg, Sr, Ba. Method: IC.

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Method: HPLC.

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Metals: Al, Ba, Cd, Cr, Cu, Fe, Pb, Mn. Method: DCP-ES.

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Method: ICP-ES.

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Method: ICP-MS.

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Method: HPLC.

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Metals: Cd. Method: AAS.

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Metals: Cu, Al, Pb, Cr, Mn, Fe, Hg, Cd, Zn, Mg, Ni. Method: MIP.

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Metals: Hg. Method: AAS-Z.

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Metals: Al, As, B, Cd, Ca, Cr, Cu, In, Fe, Pb, Le, Mg, Mn, K, Ag, Na, Zn.
Method: ICP-DCP.

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Method: WMCS-AAS.

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Method: GF-AAS.

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Metals: Ba, Ca, Na, V, Fe. Method: AFS.

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Metals: Pb, Cd. Method: AAS-EA.

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Metals: Hg. Method: AAS.

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Method: IC.

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Metals: Ag, As, Au, Hg, Pb, Se, Sn, Zn, Cd. Method: ICP-OES, AAS.

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Metals: Cu, Zn, Pb, Ni, Co, Cd, Cr, Fe, Mn, Al, Ti.

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Metals: Cr. Method: HPLC.

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Metals: Cd. Method: AAS-EA.

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Metals: Zr, Ti, Cu. Method: ICP-OES.

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Metals: Mn, Fe, Cr, Mg, Ni, V, Ca, Cu, La, Ti. Method: ICP-OES.

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Metals: Co, Cu, Ni, Fe, Te, Se, Mo, Pb, Zn, Bi. Method: TLC.

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Metals: As, Ge, Hg, Sb, Se, Te, Bi. Method: HG-ICP.

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Metals: Cd, Cu, Ni, Co, Bi, Hg. Method: HPLC.

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Method: IPC.

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Metals: Si. Method: ICP-ES.

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Method: DAI.

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Method: NSIC.

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Method: NSIC.

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Method: ICP-ES.
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Metals: As. Method: HG-AAS.
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Metals: Ni, Cu, Fe, Pb, Ag. Method: R-pPC.
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Metals: Cu, Cd, Ba, Be, Ti, Zr, Sr, Mn, Fe. Method: ICP-ES.
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APPENDIX B: LIST OF VENDORS CONTACTED FOR ANALYTICAL TECHNOLOGIES REPORT

Analect Instruments
1231 Hart St.
Utica, NY 13502
315-797-4449

Angstrom, Inc.
P.O. Box 248
Belleville, MI 48111
313-697-8058

Applied Res. Labs.
Bausch & Lomb, Inc.
9545 Wentworth St.
Sunland, CA 91040
818-352-6011

Baird-Atomic, Inc.
125 Middlesex Tnpk.
Bedford, MA 01730
617-276-6000

Beckman Instruments
2500 Harbor Blvd.
Fullerton, CA 92634
714-871-4848

Buck Scientific
58 Fort Point St.
E. Norwalk, CT 06854
203-853-9444

Cameca Instruments
2001 W. Main St.
Stamford, CT 06902
203-348-5252

Chemetrics, Inc.
Rt 28
Calverton, VA 22016
703-788-9026

Coleman Instruments
Perkin-Elmer Corp.
42 Madison St.
Maywood, IL 60153
312-345-7500

Corning Glass Works
Main Plant 21 5 8
Corning, NY 14830
607-974-9000

DIONEX Corporation
1228 Titan Way
Sunnyvale, CA 94086
408-737-0700

Fiatron Systems Inc.
6651 N. Sidney Pl.
Milwaukee, WI 53209
414-351-6650

Foreign Trade Dept.
Shimadzu Seisakusho
14-5, Uchikanda
1-chrome Chiyodaku, Japan
296-2350

Gelmarr Instruments Ct.
600 S. Wagner Road
Ann Arbor, MI 48106
800-521-5120

General Ionex Corp.
19 Graf Rd.
Newburyport, MA 01950
617-462-7147

Gilson Med. Elect.
3000 Beltline Hwy
Middleton, MI 53562
608-836-1551

INAX Instruments
Box 6044, Stn. J
Ottawa, Canada,
613-829-5068

Instrumentation Lab.
113 Hartwell Ave.
Lexington, MA 02173
617-861-0710

Instruments S A, Inc
173 Essex Ave
Metuchen, NJ 08840
201-494-8660

Interaction Chemical, Inc.
1615 Plymouth Street
Mountain View, CA 94043
415-969-2400

Ionics Inc.
65 Grove St.
Watertown, MA 01803
617-272-7233

Japan Spectroscopic
5-2967 Ishikawacho
Hachioji, Tokyo, Japan 192
042-642-9225

Jarrell-Ash Div.
Fisher Scientific
590 Lincoln Street
Waltham, MA 02254
617-890-4300

Lamotte Chem Product
Box 329
Chestertown, MD 21620
301-778-3100

Leeman Labs Inc.
600 Suffolk St.
Lowell, MA 01854
617-454-4442

Leybold-Heraeus
5700 Mellon Road
Export, PA 15632
412-327-2022

McKee-Pederson Inst.
P.O. Box 322
Danville, CA 94526
415-937-3630

Micro Filtration Systems
8 Stansbury Court
Fredricksburg, VA 22401
703-786-7315

PERCO
30 Austin Blvd
Commack, NY 11725
516-543-5580

Perfector Science
Box 91
Atascadero, CA 93423
805-466-8497

Perkin-Elmer Corp.
702-G Main Ave
Norwalk, CT 06856
203-762-6972

Phillips Elect. Inst
750 S. Fulton Ave.
Mount Vernon, NY 10550
914-664-4500

Processes and
Instruments, Corp.
1943 Broadway
Brooklyn, NY 11207
212-452-8380

Rank Precision Ind.
411 E. Jarvis Ave.
Des Plaines, IL 60018
312-297-7720

Sargent Welch Sci.
Box C-1000
Skokie, IL 60076
312-677-0600

Schoeffel/McPherson
530 Main ST.
Acton, MA 02254
617-263-7733

Science Products Division
Abbott
820 Mission St.
S. Pasadena, CA 91030
213-441-1171

Scientific Inst Div.
Nissei Sangyo Americ
460 E Middlefield Rd
Mountain View, CA 94043
800-227-8877

Scientific Resources
3300 Commercial Ave.
Northbrook, IL 60062
312-498-2920

SCIEX
55 Glencameron Rd.
Unit 202
Thornhill, ON L3T 1P2, CANADA
416-881-4646

Scintrex LTD
222 Snidercroft Rd.
Concord, ON L4K 1B5, CANADA
416-669-2280

Siemens Corp.
186 Wood Ave., S.
Iselin, NJ 08830
201-494-1000

Spectra Metrics Inc.
204 Andover St.
Andover, MA 01810
617-475-7015

Spectro, Inc.
597 Williams St.
Thornton, IL 60476
312-877-6434

Spectro Products
385 State St.
New Haven, CT 06473
203-281-0121

Spex Industries, Inc
3880 Park Ave.
Metuchen, NJ 08840
201-549-7144

The ANSPEC Company
P.O. Box 7730
Ann Arbor, MI 48107
313-665-9666

U.S. Testing Co.
1415 Park Ave.
Hoboken, NJ 07030
201-792-2400

Varian Inst. Group
220 Humbolt Ct
Sunnyvale, CA 94089
408-734-5370

Waters Associates
34 Maple St.
Milford, MA 01757
617-478-2000

Wescan Instruments, Inc.
3018 Scott Blvd.
Santa Clara, CA 95054-0984
408-727-3519

Zeebac Inc.
P.O. Box 345
Berea, OH 44017
216-243-2433

APPENDIX C: SAMPLE ACID DIGESTION TECHNIQUES

Table C1
HNO3-HCl Digestion

Step	Procedure
1	Prepare HNO3-HCl (1:3 v/v) digestion mixture (aqua regia) just prior to each use by carefully adding, with stirring, one volume conc. HNO to three volumes of conc. HCl. A convenient batch volume is a 30-ml conc. HNO3 and 90-ml conc. HCl. CAUTION: Avoid inhaling fumes.
2	Accurately weigh a 0.05- to 1.0-g dried sludge sample, using an analytical balance. Select the sample weight based on anticipated metal concentrations and the detection limit/upper concentration range of the atomic absorption spectrophotometer calibration curves.
3	Place dried sludge in an Erlenmeyer flask (125- or 250-ml volume). Alternatively, a 250-ml beaker with watch glass may be used.
4	Moisten dried sludge with ca. 0.5- to 1.0-ml deionized distilled water (DDW).
5	Slowly add 10-ml HNO3-HCl and swirl container to control effervescence and to ensure good mixing.
6	Place container on hot plate. Bring to slow boil. Continue boiling until solution approaches dryness.
7	Carefully add more HNO3-HCl in 5-ml increments and repeat Step 5 until all visible organic matter is destroyed and the solution begins to clear.
8	Continue boiling until the evolution of reddish-brown fumes ceases.
9	Remove container from hot plate, cool to room temperature, add ca. 20-ml DDW, and separate the digestate from any mineral residue, if present, by filtering through a Whatman No. 42 or equivalent filter paper or a 0.4- μ m membrane filter.
10	Rinse container and filter paper with ca. 5- to 10-ml DDW two times and collect rinses. Quantitatively transfer and combine rinses and filtrate into a volumetric flask (50- or 100-ml volume) and dilute with DDW to the volume mark.
11	Dilute the solution from Step 10 further, if necessary. Analyze metal(s) by atomic absorption spectrophotometry according to the instrument manufacturer's operating instructions. Calculate and report the concentration of metal(s) in the sludge sample on a milligrams per kilogram dry weight basis.

Table C2
HNO₃ Digestion

Step	Procedure
1	Place dried sludge in an Erlenmeyer flask (125- or 250-ml volume). Alternatively, a 250-ml beaker with watch glass may be used.
2	Moisten dried sludge with ca. 0.5- to 1.0-ml DDW.
3	Slowly add 10-ml conc. HNO ₃ and swirl container to control effervescence and to ensure good mixing.
4	Place container on hot plate. Bring to slow boil. Continue boiling until the solution approaches dryness.
5	Carefully add more conc. HNO ₃ in 5-ml increments and repeat Step 5 until all visible organic matter is destroyed and the solution begins to clear.
6	Continue boiling until the evolution of reddish-brown fumes ceases.
7	Remove container from hot plate, cool to room temperature, add ca. 20-ml DDW, and separate the digestate from any mineral residue, if present, by filtering through a Whatman No. 42 or equivalent filter paper or a 0.4- μ m membrane filter. Collect filtrate.
8	Rinse container and filter paper with ca. 5- to 10-ml DDW two times and collect rinses. Quantitatively transfer and combine rinses and filtrate into a volumetric flask (50- or 100-ml volume) and dilute with DDW to the volume mark.
9	Dilute the solution from Step 9 further, if necessary. Analyze metal(s) by atomic absorption spectrophotometry according to the instrument manufacturer's operating instructions. Calculate and report the concentration of metal(s) in the sludge sample on a milligrams per kilogram dry weight basis.

Table C3
HNO₃-H₂O₂ Digestion

Step	Procedure
1	Place dried sludge in an Erlenmeyer flask (125- or 250-ml volume). Alternatively, a 250-ml beaker with watch glass may be used.
2	Moisten dried sludge with ca. 0.5- to 1.0-ml deionized distilled water (DDW).
3	Slowly add 10-ml conc. HNO ₃ and swirl container to control effervescence and to ensure good mixing.
4	Place container on hot plate. Bring to slow boil. Continue boiling until the solution approaches dryness.
5	Carefully add more conc. HNO ₃ in 5-ml increments and repeat Step 4 until all visible organic matter is destroyed and the solution begins to clear.
6	Continue boiling until the evolution of reddish-brown fumes ceases.
7	Remove container from the hot plate and cool to ca. room temperature.
8	Add 3-ml conc. HNO ₃ and 10-ml 30-percent H ₂ O ₂ . Return container to the hot plate and warm gently. Using tongs, alternatively remove the container from the hot plate to allow any effervescence to subside and then rewarm. Continue this process until subsequent warming does not produce any further effervescence.
9	Heat the solution to boiling and continue heating for at least 15 min.
10	Remove container from hot plate, cool to room temperature, add ca. 20-ml DDW, and separate the digestate from any mineral residue, if present, by filtering through a Whatman No. 42 or equivalent filter paper or a 0.45-μ membrane filter. Collect filtrate.
11	Rinse container and filter paper with ca. 5- to 10-ml DDW two times and collect rinses. Quantitatively transfer and combine rinses and filtrate into a volumetric flask (50- or 100-ml volume) and dilute with DDW to the volume mark.
12	Dilute the solution from Step 11 further, if necessary. Analyze metal(s) by atomic absorption spectrophotometry according to the instrument manufacturer's operating instructions. Calculate and report the concentration of metal(s) in the sludge sample on a milligrams per kilogram dry weight basis.

Table C4
HF-HClO₄-HNO₃ Digestion

Step	Procedure
1	Accurately weigh a 0.5- to 1.0-g dry weight equivalent of the homogenized sample using an analytical balance. Transfer the sample to a 50-ml polypropylene beaker.
2	Add 5-ml 48-percent hydrofluoric acid (HF) and heat on a steam bath at about 100° C to dryness (8 to 12 hr).
3	Transfer residue to a 100-ml Kjeldahl flask. Add 10-ml digestion solution (5 parts conc. HNO ₃ and 3 parts 60-percent HClO ₄). Heat on an Aminco (American Instrument Company) micro Kjeldahl unit until the evolution of HClO ₄ fumes. This step should be performed in an appropriate fume hood, and a trap should be established to catch the HClO ₄ fumes.
4	Add 5-ml conc. HCl and heat for 1 hr.
5	Cool the sample. Dilute to approximately 30 ml with distilled water.
6	Filter to remove any solid residue and dilute to 100 ml or some other convenient volume with distilled water. Analyze by the method of choice.

Table C5
HF-HNO₃-HCl Digestion

Step	Procedure
1	Accurately weigh 0.1- to 0.5-g dry weight equivalent of homogenized sediment using an analytical balance. Transfer to a PTFE bomb (Pan 4745 acid-digestion bomb or equivalent; Pan Instrument Company, Moline, Ill.).
2	Add 6-ml 48-percent HF and 1-ml aqua regia (3:1 HCl:HNO ₃). Seal the bomb and heat at 110° C for 2 hr.
3	Cool the samples and transfer to a 125-ml polypropylene wide-mouthed bottle containing 4.8-g boric acid.
4	The digestate can be analyzed for metals except mercury by transferring to a volumetric flask, adding 10-ml hydroxylammonium sulfate 6-percent m/v sodium chloride), and diluting to volume. Analyze by method of choice.
5	To analyze the digestate for mercury, cool the sample bomb in an ice-water bath. Carefully add 10-ml 6-percent m/v potassium permanganate and let stand 30 min.
6	Add 5-ml 5-percent potassium persulfate and allow samples to digest overnight at room temperature.
7	Transfer to a volumetric flask. Add 10-ml hydroxylammonium sulfate-sodium chloride solution (6-percent m/v hydroxylammonium sulfate 6-percent m/v sodium chloride) and dilute to volume. Analyze by method of choice.

APPENDIX D: SAMPLE ASHING TECHNIQUES

Table D1
Muffle Furnace Ignition

Step	Procedure
1	Place the Pt crucible containing the dried sludge sample into a room temperature muffle furnace. Bring the furnace to 550° C and maintain the temperature for ca. 30 min.
2	Remove the Pt crucible from the muffle furnace, cool for 5 to 10 min, place in a desiccator, and cool to room temperature. Reweigh the crucible, if desired, to determine the amount of volatile matter lost on ignition.
3	Add a small volume (1 to 3 ml) of warm conc. HNO_3 to the residue in the Pt crucible and place on a hot plate. Heat the crucible (avoid splattering and do not boil) until most of the acid has evaporated. Do not heat to dryness.
4	Remove container from hot plate, cool to room temperature, add ca. 20-ml deionized distilled water (DDW), and separate the digestate from any mineral residue, if present, by filtering through a Whatman No. 42 or equivalent filter paper or a 0.4- μ membrane filter. Collect filtrate.
5	Rinse container and filter paper with ca. 5- to 10-ml DDW two times and collect rinses. Quantitatively transfer and combine rinses and filtrate into a volumetric flask (50- or 100-ml volume) and dilute with DDW to the volume mark.
6	Dilute the solution from Step 5 further, if necessary. Analyze metal(s) by atomic absorption spectrophotometry according to the instrument manufacturer's operating instructions. Calculate and report the concentration of metal(s) in the sludge sample on a milligrams per kilogram dry weight basis.

Table D2
Low Temperature Ashing

<u>Step</u>	<u>Procedure</u>
1	Place the Petri dish containing the dried sludge sample into the low temperature ashing instrument cavity and operate according to the instruction manual. A flat quartz plate can be installed in cylindrical cavities for ease of sample placement. Experience shows that three successive 8-hr ashing cycles at 200 W (RF) are necessary to completely ash the sludge sample.
2	Upon completion of the ashing step, dissolve the residue with a small volume (ca. 1 to 3 ml) of conc. HNO_3 and quantitatively transfer the solution to a filtration apparatus, if necessary.
3	Rinse container and filter paper with ca. 5- to 10-ml DDW two times and collect rinses. Quantitatively transfer and combine rinses and filtrate into a volumetric flask (50- to 100-ml volume) and dilute with DDW to the volume mark.
4	Dilute the solution from Step 3 further, if necessary. Analyze metal(s) by atomic absorption spectrophotometry according to the instrument manufacturer's operating instructions. Calculate and report the concentration of metal(s) in the sludge sample on a milligrams per kilogram dry weight basis.

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